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In situ DRIFTS studies of high-temperature water-gas shift reaction on chromium-free iron oxide catalysts

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ABSTRACT

The identification of reaction surface intermediates in the high-temperature water-gas shift reaction on iron oxide unpromoted and promoted MgO, SiO₂ and TiO₂ has been studied via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The dosing of the gas mixture CO + H₂O onto reduced Fe₂O₃/MgO as a function of reaction temperature produced formate species (1720, 1630 and 1370 cm⁻¹) as a surface intermediate. On reduced Fe₂O₃/TiO₂ only bands characteristic of carbonate species (1630 and 1550 cm⁻¹) are observed. A direct correlation between catalytic activity and acid/base properties of our catalysts is established. The Fe₂O₃/MgO basic catalyst is 100 times more active than the acidic catalyst Fe₂O₃/SiO₂.

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R É S U M É

L'identification des intermédiaires de surface en réaction de conversion du gaz à l'eau, dans le domaine des hautes températures, sur l'oxyde de fer seul et supporté par MgO, SiO₂ et TiO₂ a été étudiée par spectroscopie infrarouge en réflexion diffuse (DRIFTS). Le dosage de Fe₂O₃/MgO par le mélange gazeux CO + H₂O en fonction de la température de réaction alimente la surface en espèces formates (1720, 1630 et 1370 cm⁻¹). Sur le système Fe₂O₃/TiO₂, seules les bandes caractéristiques des espèces carbonates (1630 et 1550 cm⁻¹) sont observées. Une corrélation directe entre l'activité catalytique et les propriétés acido-basiques est établie. Le catalyseur basique Fe₂O₃/MgO est 100 fois plus actif que le catalyseur acide Fe₂O₃/SiO₂.

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1. Introduction

The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is generally operated according to a two-step process, namely at high (HTS, 350–450 °C) and low (LTS, 250–300 °C) temperatures, over two main types of catalysts, Fe-Cr and Cu-Zn systems, respectively. Iron oxide based HTS

catalysts, Fe₃O₄ [1,2] or Fe₂O₃ [3], are generally doped with Cr₂O₃ [4–7]. The recognized role of chromium is preventing iron oxide from sintering as well as catalyzing the WGS reaction. However, catalysts based on Fe-Cr-O have ecological and safety problems linked to chromium compounds. For this reason, development of chromium-free iron-based catalysts with high HTS performance is suitable [3,8,9].

The WGS reaction is thought to occur principally through two main types of mechanisms, the regenerative or redox mechanism [1,10] and the associative mechanism

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[1]. In the regenerative mechanism the catalyst surface is successively oxidized by H_2O and reduced by CO . In turn, the associative mechanism assumes that CO and H_2O interact to form a reaction intermediate, such as an adsorbed formate species, which then decomposes to CO_2 and H_2 . It was found by Rethwisch and Dumesic [1] that Fe_3O_4 catalyzed the water-gas shift reaction via the regenerative mechanism while MgFe_2O_4 , ZnO , MgO , TiO_2 , SiO_2 catalyzed the water-gas shift reaction mainly via the associative mechanism. It was also established that basic oxides were more active than acidic or amphoprotic ones. This can be related to the weaker metal-oxygen bonding in basic oxides.

The associative mechanism generally considers a kind of bifunctional sequence with a specific role of metal and support. Thus, the formate can form from the surface reaction of CO bonded to the metal with OH groups located at the metal-support interface, as follows: $\text{CO}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{HCOO}_{\text{ad}}$. The formate bonded on the metal then spills over to the support where it decomposes to CO_2 and H_2 [11].

In the present paper, we give the effect of the acid/base properties of various supports on chromium-free iron-based catalyst in the WGS Reaction. Besides the determination of catalytic activity and acid/base properties, catalysts were subjected to in situ DRIFT measurements in order to obtain the type of active sites and the part of these interfaces in the water gas shift reaction.

2. Experimental

2.1. Catalysts preparation

$\text{Fe}_2\text{O}_3/\text{SiO}_2$, $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{MgO}$ systems were prepared by the incipient wetness impregnation method. The 30 wt.% Fe_2O_3 /support catalysts were prepared by impregnation of SiO_2 , TiO_2 or MgO with an appropriate concentration of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$. After drying at 80°C overnight, the resulting solid was calcined in air at 400°C for 2.5 h [12].

Bulk Fe_2O_3 catalyst was synthesized by the coprecipitation method. The starting reagents of high purity $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$ with a molar ratio (1/1) were dissolved in water to which 100 mL of NH_4OH was added as a precipitant agent. The mixture was vigorously stirred for 30 min. The resulting powder was washed several times with deionized water, and dried at 110°C . Subsequently, the powder was calcined at 400°C in air (33 mL/min) with a rate of $5^\circ\text{C}/\text{min}$ for 2.5 h [9].

2.2. Apparatus and procedure

X-ray powder diffraction patterns were obtained with a Philips PW 1050/81 automated powder goniometer, equipped with diffracted-beam graphite monochromatic Cu (K_α) radiation.

H_2 -TPR profiles were determined using a laboratory-made apparatus equipped with a TCD detector. The catalyst sample (200 mg) was loaded into a U-shape quartz reactor, then heated at 200°C under argon flow with a rate of $5^\circ\text{C}/\text{min}$ for 1 h and cooled to room

temperature. Next, the sample was submitted to a flow of 5% H_2/Ar from room temperature to 800°C . A cold trap was placed downstream of the sample to capture any water that evolved from catalyst prior to entering the TCD detector.

Catalysts were tested under atmospheric pressure between 350 and 450°C after being activated in situ under a flow of 48% H_2/N_2 using an amount of catalyst of 250 mg for all runs. After reduction, the reacting gases ($\text{H}_2\text{O}/\text{CO} = 4.4$) were introduced into the reactor at a total flow rate of 33 mL/min. Before each analysis, the effluent passed through a water-trap at 0°C to remove the water of the reaction. The gas composition was analyzed by a TCD chromatograph containing two 4 m carbosieve B columns (1/8 inch, 100 to 200 meshes).

In situ DRIFT studies were performed on a Nicolet Magna IRTF spectrometer with OMNIC software. The reaction was performed in a high temperature Spectra-TECH cell equipped with a ZnSe window. The sample (~ 50 mg) was first treated in a flow of (~ 35 mL/min) H_2 at 400°C for 30 min (high-temperature treatment) before each experiment. The heating rate during the treatment was $10^\circ\text{C}/\text{min}$. After this treatment, the sample was cooled under He and then put in contact with the reacting mixture $\text{CO}/\text{H}_2\text{O}$ at increasing temperature (25 – 450°C). Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were recorded with co-addition of 64 scans in single-beam spectra or absorbance spectra, by applying a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. XRD and H_2 -TPR measurements

The X-ray phases of Fe_2O_3 -only and Fe_2O_3 -promoted freshly calcined samples are given in Table 1. α - Fe_2O_3 hematite is the mainly crystalline phase in Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$. For the system doped with MgO , at higher Fe_2O_3 loading (30 wt.%) the band characteristic of MgO decreased while new bands assigned to MgFe_2O_4 are formed [9]. This indicates that iron oxide is in strong interaction with MgO , leading to a mixed oxide formation.

H_2 -TPR results of the four catalysts are reported in Fig. 1 and their peak maxima are summarized in Table 1. In all cases, three peaks of hydrogen consumption in a temperature range of 25 – 800°C are observed [13,14]. For Fe_2O_3 -only, the lower reduction temperature region (446°C) of Fe_2O_3 is attributed to the reduction of Fe_2O_3 to Fe_3O_4 while the higher temperature region (606 – 684°C) is credited to the reduction of Fe_3O_4 to FeO and Fe . The low temperature peaks of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{MgO}$ shifted to 340 and 368°C respectively. On the other hand, MgO -promoted catalyst involved a shift of the reduction temperature to lower values as depicted in Fig. 1, curve c. XRD studies showed that MgFe_2O_4 crystalline phase is present in $\text{Fe}_2\text{O}_3/\text{MgO}$. Indeed, the presence of this phase improves the reducibility of $\text{Fe}_2\text{O}_3/\text{MgO}$. More detailed studies were reported elsewhere [9].

Table 1
Characterization results and CO conversion of catalysts prepared.

Sample	S BET (m ² /g)	XRD ^a phases	H ₂ -TPR T _{max} (°C)	Acid/base properties ^b		Rate of CO conv. to CO ₂ at 450 °C (mol/m ² cat. s × 10 ⁵) ^c
				S _{C₃H₆O} (%)	S _{C₃H₆} (%)	
Fe ₂ O ₃	25.0	α-Fe ₂ O ₃	446, 607, 684	58	42	0.14
Fe ₂ O ₃ /SiO ₂	90.7	α-Fe ₂ O ₃ , SiO ₂	500, 600, 680	18	82	0.03
Fe ₂ O ₃ /TiO ₂	14.0	α-Fe ₂ O ₃ , TiO ₂	340, 430, 620	82	18	0.25
Fe ₂ O ₃ /MgO	02.2	MgFe ₂ O ₄ , MgO	368 ^d , 421, 431	92	8	3.00

^a Freshly calcined catalyst.

^b Selectivity after C₃H₇OH decomposition at a temperature of 250 °C, using 100 mg of reduced catalyst.

^c At a temperature reaction (CO + H₂O) of 450 °C.

^d Shoulder.

3.2. Catalytic properties in CO + H₂O reaction

The only products of the WGS reaction were found to be carbon dioxide and hydrogen, no methane being detected. No reaction occurred on every support alone. The WGS reaction conversion of the tested catalysts (unsupported and supported Fe₂O₃) was expressed by the conversion of CO to CO₂, measured at 450 °C, and expressed per surface area unit, as presented in Table 1. The specific activity appears to span over a large range, the most active system (Fe₂O₃/MgO) displaying a rate 100 times higher more than the least active (Fe₂O₃/SiO₂). The four tested systems were ranked as follows: Fe₂O₃/MgO >> Fe₂O₃/TiO₂ > Fe₂O₃ >> Fe₂O₃/SiO₂. The activation energy was estimated to be 97.6 kJ/mol in the temperature range of 350–450 °C over the Fe₂O₃/MgO catalyst. This value is in accord with the value reported by Rethwisch et al. (106 kJ/mol) [1].

As can be seen in Table 1 and Fig. 2, a direct relationship can be observed between catalytic activity and acid/base properties of our catalysts: Fe₂O₃/MgO >> Fe₂O₃/TiO₂ > Fe₂O₃ >> Fe₂O₃/SiO₂. Basic properties of catalysts are given here in terms of dehydrogenation of isopropanol: CH₃-CHOH-CH₃ → CH₃-CO-CH₃ + H₂ at a temperature reaction of 250 °C [12]. The dependence found that oxides which are basic were more active than those which are

acidic or amphoteric and can be explained in terms of the higher activity of surface species like formates [1]. It is suggested, by these authors, that formate species readily formed and dehydrogenated to provide CO₂ and H₂.

One can see that the increase in intensity of the 2420–2330 cm⁻¹ band (Fig. 3b–d), as well as the decrease of formate species bands with raising the temperature to 450 °C illustrated the decomposition of adsorbed HCOO species to CO₂ and H₂ [11]. This decomposition is facilitated by the weaker metal-oxygen bond in the basic oxides. In the opposite, on an acidic sample, such as Fe₂O₃/SiO₂, no formate intermediates were detected and the intrinsic rate was the lowest of the four systems.

3.3. In situ DRIFT study of surface species

Fig. 3 shows the change in DRIFT spectra recorded for the Fe₂O₃/MgO system after reduction and after contact with the CO/H₂O gas mixture at increasing reaction temperatures. The spectrum (b), recorded after exposure of the reduced catalyst to CO/H₂O at 350 °C, showed a very prominent broad OH adsorption band with a maximum at about 3570 cm⁻¹; as expected from H₂O interaction with mild basic OH groups of MgO surface along with a sharp band at 3730 cm⁻¹ typical of isolated basic Mg(OH) groups

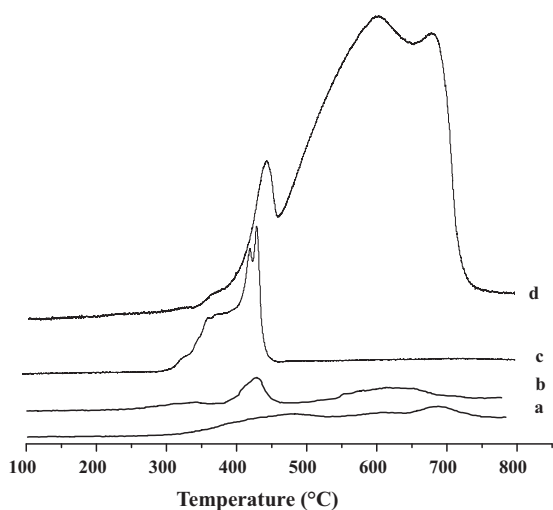


Fig. 1. H₂-TPR Profiles of freshly calcined samples: a: 30 wt.% Fe₂O₃/SiO₂; b: 30 wt.% Fe₂O₃/TiO₂; c: 30 wt.% Fe₂O₃/MgO and d: Fe₂O₃.

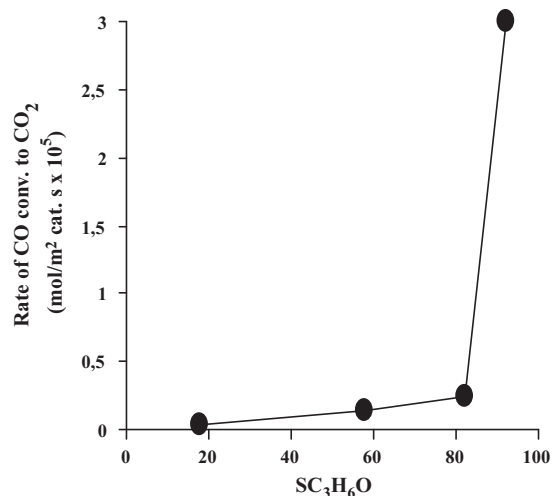


Fig. 2. Evolution of the rate of CO conversion to CO₂ as a function of basic properties of our prepared catalysts (expressed in term of dehydrogenation of isopropanol C₃H₇OH at 250 °C. P_{isopropanol} = 1.080 kPa [12]).

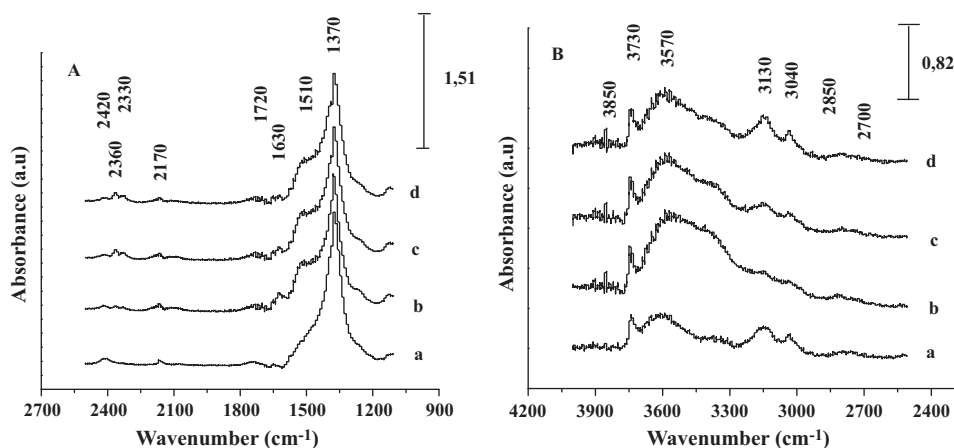


Fig. 3. DRIFTS spectra of the $\text{Fe}_2\text{O}_3/\text{MgO}$ system recorded (a) at RT after reduction, (b) under $\text{CO}/\text{H}_2\text{O}$ reaction conditions at 350 °C, (c) 400 °C and (d) 450 °C.

over the surface. Other OH bands are observed at 3130, and 3040 cm^{-1} which might be assigned to acidic FeOH groups. Moreover, small bands are seen around 2170–2080 cm^{-1} and in the 2420–2330 cm^{-1} region. The 2170–2080 cm^{-1} bands are characteristic of the CO gaseous while the doublet at the 2400–2330 cm^{-1} region corresponds to adsorbed and/or gaseous CO_2 rotation-vibration P and R bands. The increase of the latter with temperature attests that the shift reaction does proceed in the DRIFT reactor, in line with the outlet gas analysis. The inlet of $\text{CO}/\text{H}_2\text{O}$ on reduced $\text{Fe}_2\text{O}_3/\text{MgO}$ produces, as well as at 350 °C, bands at 1720, 1630, and 1370 cm^{-1} , which diminished synchronously by increasing temperature from 350 to 450 °C. The synchronic dynamics of these 3 bands tends to indicate that they arose from the same OCO containing species. By observing simultaneously some C-H stretching vibrations at 2850–2700 cm^{-1} associated with the 1720, 1630, and 1370 cm^{-1} OCO region bands, we propose, in agreement with Tabakova et al. [15], that the diminution of the band at 2170 cm^{-1} as well as the decrease in intensity of the OH band at 3570 cm^{-1} (from 350 to 450 °C) can be correlated with the production of formate species. As a matter of fact, formate species involve symmetric and asymmetric OCO band vibrations on the surface of the catalyst. The asymmetric OCO band is expected at 1580 cm^{-1} [15,16], and the symmetric one at 1375 cm^{-1} . The vibrations of the OCO bands are accompanied by C-H stretching vibrations at 2850–2700 cm^{-1} .

In other terms, it is proposed that the carbonyl adspecies bonded to iron sites might react with the magnesia basic OH groups located at the metal-support interface to produce formate intermediate species. Formate adspecies are often considered as active intermediates in the water-gas shift reaction over supported metals and also on support alone [1,11,17,18] and more precisely over MgFe_2O_4 in [1] or over pure MgO in [19].

Fig. 4 reports the DRIFT spectra of the reduced $\text{Fe}_2\text{O}_3/\text{TiO}_2$ system after exposure to the $\text{CO}/\text{H}_2\text{O}$ gas mixture at increasing temperature. At variance with the previously reported system, no significant IR contribution from formate species was observed on the reduced $\text{Fe}_2\text{O}_3/\text{TiO}_2$ catalyst after being contacted with $\text{CO}/\text{H}_2\text{O}$. This can be

deduced from the absence of vibration characteristic of C-H bonds in the 2850–2700 cm^{-1} range. In line with this observation, only weak formate bands were observed on TiO_2 by Rethwisch and Dumesic [1]. The broad band at 3410 cm^{-1} observed essentially at 350 °C, and then decreasing at higher temperature, is characteristic of Ti-OH hydroxyl groups. After contacting $\text{Fe}_2\text{O}_3/\text{TiO}_2$ at 350 °C with $\text{CO}/\text{H}_2\text{O}$ gases, two new bands are detected in the carbonate/carboxylate species region, specifically at 1630 and 1550 cm^{-1} [20]. In addition, Fig. 4 (curve a) shows the doublet at 2170–2080 cm^{-1} characteristic of the CO gaseous together with the doublet at ~ 2370 and 2320 cm^{-1} characteristic of adsorbed and/or gaseous CO_2 [20,21]. By increasing temperature the intensities of the bands at 3410 cm^{-1} , at 2080–2170 cm^{-1} , at 1630 and at 1550 cm^{-1} decreased but the intensity of the bands at 2370–2320 cm^{-1} increased. These trends indicate that while WGS proceeds, the surface is progressively depleted in adsorbed species while the gaseous CO concentration increases. Therefore, no clear evidence of a WGS route via formate intermediates was obtained for this case of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ catalyst. The weaker basicity of the TiO_2 surface and/

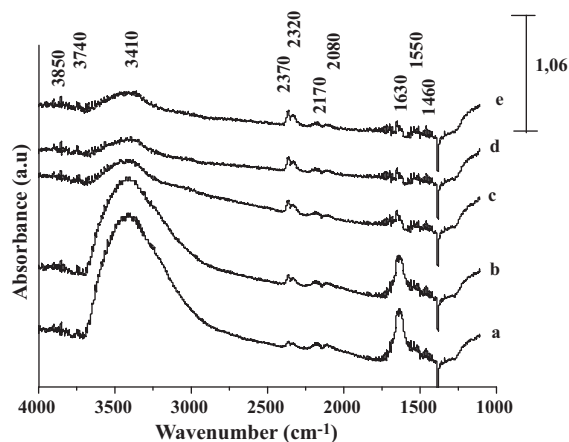


Fig. 4. DRIFT spectra of the reaction gaseous $\text{CO}/\text{H}_2\text{O}$ on $\text{Fe}_2\text{O}_3/\text{TiO}_2$ at various reaction temperatures, a: 350 °C; b: 370 °C; c: 400 °C; d: 420 °C and e: 450 °C.

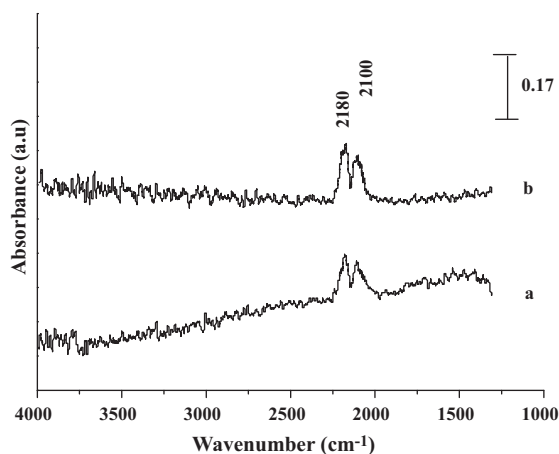


Fig. 5. DRIFT spectra of the reaction gaseous CO/H₂O on (a) Fe₂O₃ and (b) Fe₂O₃/SiO₂ under 5% CO at 450 °C.

or an inadequate interface between metal and oxide phases might be the origin of this statement.

Reduced Fe₂O₃ and Fe₂O₃/SiO₂ (Fig. 5) catalysts produced spectroscopic features significantly different from those of Fe₂O₃/MgO and Fe₂O₃/TiO₂, since no formate or carbonate bands were observed either on the unsupported system or on the silica supported one. This statement quite agrees with the expected feature that no formate/carbonate species can form on an acid oxide (silica or magnetite), under any conditions, in line with [1,11]. Therefore, it might be inferred that a redox or regenerative shift mechanism is likely to apply for these two cases, as proposed over magnetite in [1]. We note in addition that no sufficiently resolved IR spectra could be recorded for this last case due to sample black color after reduction.

4. Conclusions

Fe₂O₃/MgO, Fe₂O₃/TiO₂, Fe₂O₃ and Fe₂O₃/SiO₂ are active in high temperature WGS Reaction.

A direct correlation between catalytic activity and acid/base properties of the prepared catalysts is found.

The Fe₂O₃/MgO basic catalyst is 100 times more active than the acidic catalyst Fe₂O₃/SiO₂.

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