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An environmental friendly dopant for the high-temperature shift catalysts

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Abstract

The high-temperature shift (HTS) reaction is an important step in industrial processes and gas purification. Although the catalyst shows a stable performance, the search for non-toxic systems is much needed, especially due to environmental restrictions related to chromium compounds. In this work, the performance of aluminum-doped catalysts with low amounts of copper was investigated, because of the role of copper on decreasing the surface area of the catalysts based on iron oxides. Samples were prepared by precipitation methods, characterized by several techniques and evaluated under different conditions, in order to find operational conditions more effective in the use of energy.

The addition of small amounts of copper to aluminum-doped hematite leads to better catalytic properties. Likely, copper behaves as a structural promoter while aluminum is a textural one. The catalyst can work at more severe conditions than the industrial condition, that is, lower steam to gas molar ratio ($S/G = 0.4$) and at a lower temperature (350°C). In addition, it can be easily handled and discarded without any damage to the environment or human beings. © 2000 Published by Elsevier Science B.V.

Keywords: Environmental friendly dopant; Shift reaction; Magnetite

1. Introduction

The water-gas shift reaction (WGSR) is widely used in the industrial production of hydrogen, either for the manufacture of ammonia or for the adjustment of the carbon monoxide to hydrogen ratio in the synthesis gas for several applications [1]. In these cases, the hydrogen is primarily obtained by the reforming of methane or higher hydrocarbons, a reaction that produces carbon monoxide and hydrogen as main products. Because the hydrogen concentration in the product gas is low, the WGSR is used to increase the hydrogen production. Furthermore, it simultaneously reduces the carbon oxides to very low levels, thus avoiding the poisoning of the ammonia-synthesis catalysts or the most metallic hydrogenation catalysts [2].

On the basis of thermodynamic considerations, the WGSR is often performed in two steps, namely high-temperature stage, at temperatures in the range of 623–723 K, and in a second low-temperature stage, in the range of 453–523 K [1,3,4]. The first stage involves an iron chromium catalyst, which decreases the carbon monoxide concentration from ca. 10 mol% (for natural gas derived synthesis gas) to ca. 3 mol%, at kinetic favorable conditions. In the second step, the carbon monoxide concentration is further decreased to ca. 0.3 mol%, using a copper zinc oxide low-temperature shift catalyst [1,3].

Most industrial high-temperature shift (HTS) catalysts contain iron oxide, as well as chromium oxide which is believed to act as a stabilizer, retarding sintering and loss of surface area [1–3].

In spite of the chromium-doped hematite catalysts have shown high stability in performance, they

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have been recently modified by the addition of small amounts of copper, resulting in even more active and selective catalysts. These solids are in commercial use but there is no information about them in the open literature. However, because of environmental restrictions concerning the discarding of chromium compounds, the search for non-toxic catalysts, that can be easily handled and discarded, is much needed.

In a previous work [5] we had shown that aluminum could be a convenient option to replace chromium in copper-based HTS catalysts, operating in conditions similar to the industrial ones (at 370°C and at a steam to gas molar ratio of 0.6). These solids contain about 8% in copper which make them more susceptible to lose surface area, since it was noted [6] that copper favors sinterization of catalysts based on iron oxides. The loss of surface area leads to slow deactivation of the catalyst, as noted in industrial processes [7]. Therefore, it is important to investigate solids with lower amounts of copper and his behavior at different conditions of temperature and steam to gas molar ratio (*S*/*G*).

With this goal in mind, this work deals with the replacement of chromium by aluminum in HTS catalysts with small amounts of copper. In order to save the energy related to the steam consumption, and to the reactor temperature, the catalysts were also evaluated in more severe operational conditions than the industrial ones, e.g. lower steam to carbon ratios as well as lower temperatures.

2. Experimental

2.1. Catalyst preparation

Reagents used were analytical grade. The catalysts were prepared by precipitation techniques at room temperature, followed by heating at 500°C for 2 h under nitrogen flow (100 ml min^{-1}). Four samples were prepared: (i) with aluminum and copper (IAC sample); (ii) only with aluminum (IA sample); (iii) only with copper (IC sample) and (iv) without any dopant (I sample). An iron to aluminum molar ratio of 10 and an iron to copper molar ratio of 20 were used in the sample preparation.

The aluminum and copper-based catalyst was prepared by adding, under stirring, aqueous solutions of $Fe(NO_3)_3·9H_2O$ (1 N) and $Al(NO_3)_3·9H_2O$ (0.1 N) and a concentrated (25%, w/w) aqueous solution of ammonium hydroxide to a beaker with water. The final pH was adjusted to 11 and the system was kept under stirring for additional 30 min. The sol produced was centrifuged (2000 rpm, 5 min) followed by a water rinsing to remove the nitrate ions from the starting material. After a second centrifugation step, the gel was impregnated with an aqueous solution of $Cu(NO_3)_2·3H_2O$ (0.008 N) for 24 h under stirring, centrifuged again and dried in an oven at 120°C. The same procedure was used to prepare the other samples. For the catalysts without copper, the gel was kept in pure water for 24 h, under stirring, in order to produce the same experimental conditions used to prepare the other samples.

2.2. Catalyst characterization

The qualitative analysis of nitrate was performed by adding about 1 ml of concentrated sulfuric acid to 10 ml of the sobrenadant after centrifugation. The formation of $[Fe(NO)]^{2+}$ was detected by a brown ring [8]. The absence of nitrate in the solid was confirmed by infrared spectroscopy in the range of 4000–650 cm^{-1} using a model IR-430 Shimadzu spectrometer and KI discs. The metal contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES) by using a model Arl 3410 machine. X-ray diffractograms were recorded at room temperature with a Shimadzu model XD3A instrument using Cu Kα radiation generated at 30 kV and 20 mA. The surface area (BET method) was measured in a Micromeritics model TPD/TPO 2900 equipment on samples previously heated under nitrogen (150°C, 2 h). The temperature programmed reduction (TPR) was performed in the same equipment, using a 5% H_2/N_2 mixture. X-ray microanalysis (XRM) was performed in a Noran microprobe coupled to a model JSM-T300 microscope operating at 20–30 kV.

2.3. Catalytic activity

The catalyst performance was evaluated using 0.2 cm^3 of powder within -50 and $+325$ mesh size, and a fixed bed microreactor consisting of a stainless

Table 1
Elemental analysis results of pure iron oxide (I sample), aluminum-doped iron oxide (IA), copper-doped iron oxide (IC) and aluminum and copper-doped iron oxide (IAC)

Sample	%Fe (+0.05)	%Al (+0.03)	%Cu (+0.03)	Fe/Al (molar) (+0.05)	Fe/Cu (molar) (+0.05)
I	70.66	–	–	–	–
IA	66.18	3.22	–	9.96	–
IC	68.58	–	3.28	–	20.91
IAC	62.16	3.15	2.76	9.51	25.62

tube, providing there is no diffusion effect. All experiments were carried out under isothermal condition and at atmospheric pressure, using a gas mixture with composition around 10% CO, 10% CO_2, 60% H_2 and 20% N_2. The catalysts were reduced during the reactor start-up like in industrial processes [2] and showed activity just after few minutes of reaction. It was used several steam to gas molar ratios (*S*/*G*): 0.2, 0.4 and 0.6, and several temperatures: 350, 370 and 400°C. The gaseous effluent was analyzed by on line gas chromatography, using a CG-35 instrument. A commercial catalyst, based on chromium, copper and iron oxides, was used to compare the performance of the samples prepared in this work. After each experiment, the Fe(II) and Fe(III) contents in the catalysts were determined to follow the iron reduction under reaction atmosphere. For the Fe(II) analysis, samples were dissolved in concentrated chloridric acid, under carbon dioxide atmosphere and then titrated with potassium dichromate [8].

3. Results and discussion

Table 1 shows the results of the analysis of iron, aluminum and copper. We can see that in the copper-doped sample, the experimental Fe/Cu ratio is close to the initial ratio, while for the aluminum-doped sample the experimental Fe/Al ratio is higher than the initial one. That result means that the adsorption of copper is decreased due to the presence of aluminum in the iron particles.

Hematite was detected in the fresh catalysts (Fig. 1a) while magnetite was found in the spent catalysts (Fig. 1b). All peaks were due to these oxides in each case. Furthermore, it can be noted that both dopants do not significantly affect crystallization. No other phase besides hematite and magnetite was detected. As aluminum and copper have ionic radius similar to the iron atom, they are expected to go into the magnetite lattice [9,10] rather than to segregate as another phase.

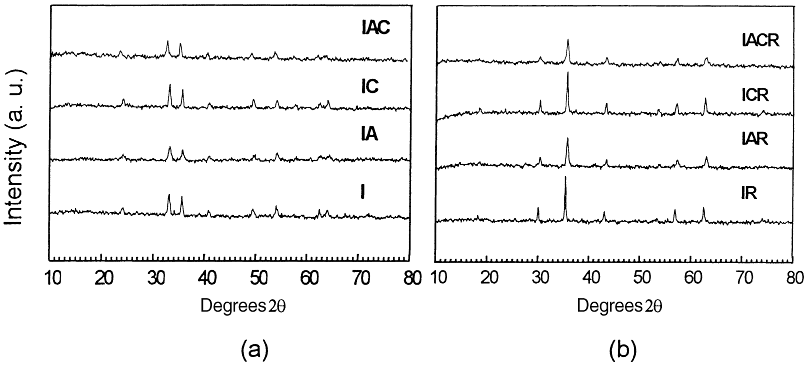

Fig. 1. X-ray diffractograms of (a) fresh and (b) spent catalysts. I sample: pure iron oxide; IA and IC: aluminum and copper-doped sample, respectively; IAC: aluminum and copper-doped sample. R represents the reduced catalysts.

Table 2
Surface area (Sg) of pure iron oxide (I sample), aluminum-doped iron oxide (IA), copper-doped iron oxide (IC), aluminum and copper-doped iron oxide (IAC) and of a commercial catalyst before and after the catalytic tests at different steam to gas molar ratio (*S*/*G*)

Sample	Sg ($m^2 g^{-1}$) (fresh catalysts)	Sg ($m^2 g^{-1}$) (reduced catalysts)			
		$S/G = 0.0$	$S/G = 0.2$	$S/G = 0.4$	$S/G = 0.6$
I	27	13	9	9	8
IA	59	43	28	25	24
IC	30	16	8	10	8
IAC	75	42	27	25	23
Commercial	58	48	30	32	13

The presence of either aluminum or the two dopants increased the surface area of the fresh catalysts (Table 2), conversely doping the solid with copper alone did not affect the surface area. The same tendency was noted for the used catalysts. These results are in accordance with previous works [11–13] about the role of aluminum as a textural promoter in several catalysts. This action has been traditionally associated with a surface phenomenon in which aluminum acts as a spacer, keeping the particles apart from each other [13]. However, Topsoe et al. [12] have shown that, in ammonia catalysts, a large fraction of aluminum is inside the iron particles as an occluded phase. Thus, aluminum causes strains in the lattice and shifts the equilibrium particle size toward smaller particles, since the ratio of strain to the surface effects becomes greater for larger particles. Table 3 shows the analysis of the bulk of the solids by ICP/AES and the analysis of the layers near the surface by XRM. From the results, it can be noted that most of aluminum is present in the bulk, therefore the chief effect seems to be related to strains in the lattice. Also, it can be seen that both aluminum and copper tend to go to the bulk of the solid due to reduction.

The catalyst reduction strongly decreased the surface area, even in the absence of steam ($S/G = 0$), showing that the phase change is followed by a coalescence of particles and/or porous. In the presence of steam the areas tend to decrease showing that steam favors sinterization. The commercial catalyst showed a similar behavior. The characteristics of the spent catalysts did not show any significant dependence on the steam to gas molar ratio (*S*/*G*) used in the test reaction. On the other hand, the surface area of the commercial catalyst decreased at $S/G = 0.6$. The surface areas of the solids were lower than the traditional chromium-doped catalysts, reported by several authors as 70–100 $m^2 g^{-1}$ [2,3]. However, the commercial copper and chromium-based catalyst showed a lower area, as shown in Table 2. This can be assigned to the copper as we had concluded in a previous work [7]. In the reduced form, the IAC sample showed an area close to the commercial catalysts, except at $S/G = 0.6$.

Table 3
XRM and ICP/AES results of the fresh (IAC sample) and reduced (IACR) aluminum and copper-doped iron oxide

Sample	Fe/Al		Fe/Cu	
	ICP/AES	XRM	ICP/AES	XRM
IAC	9.51	6.24	25.62	33.84
IACR	9.51	11.77	25.62	45.42

The TPR curves of hematite (Fig. 2) showed one peak at 510°C, due to magnetite formation, and another around 770°C, attributed to the formation of metallic iron [14]. In the aluminum-doped sample, the first peak was shifted to lower temperatures (400°C), whereas the higher temperature peak was not affected; this behavior shows that this metal eases the formation of the active phase but does not affect its stability. The copper-doped catalyst showed a TPR curve with a peak around 190°C, assigned to metallic copper [15], and other peaks around 225 and 600°C; these TPR peaks show that copper favors the active phase formation and destruction. The aluminum and copper-doped solid showed a curve with the characteristic peak due to magnetite formation displaced to 300°C and the peak related to metallic iron at 770°C. It means that the synergetic effect of the dopants is to ease magnetite formation, but not to affect the

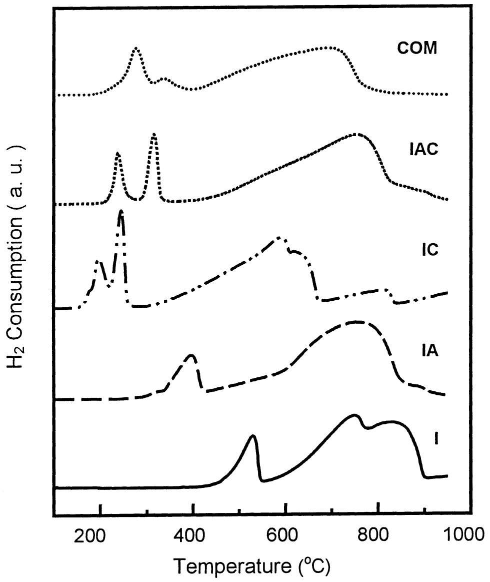

Fig. 2. TPR curves of pure iron oxide (I sample), aluminum-doped iron oxide (IA), copper-doped sample (IC), aluminum and copper-doped sample (IAC) and a commercial catalyst (COM).

production of metallic iron. The commercial catalyst exhibits TPR curves with peaks around 270, 340 and 750°C, showing that chromium is less effective in preventing the active phase formation and destruction.

All catalysts were active to HTS reaction, as shown in Table 4. The definition of activity, used in this work, considers the number of moles of carbon monoxide that reacts per hour and per gram of catalyst. Aluminum leads to a slight increase in activity, which is due to a textural effect. On the other hand, copper increased both the activity and the activity per area, showing that it acts as a structural promoter. The TPR results shows that the higher activity of the copper-promoted catalysts is due to its ability in favoring the formation and stability of the active phase (magnetite). Although copper is also active to the shift reaction, the high temperature (370°C) of the HTS step may lead to sinterization and thus copper would only cause a light increase in the activity. In addition, the results of Table 3 showed that most of copper is in the bulk. The high increase observed in performance of the catalysts suggests that copper itself has not a significant role as active site but rather as a promoter.

The increased activity of the copper-doped catalysts may be due to the two mechanisms discussed in the literature. In the regenerative mechanism [16], the surface undergoes successive oxidation and reduction cycles by water and carbon monoxide, respectively, to form the corresponding hydrogen and carbon monoxide products. The conditions for this transition are more favorable in the copper-doped solids, as shown by the TPR results, from which we can see that copper favors magnetite formation. In the adsorptive mechanism [17], reactants adsorb on the catalyst surface, where they react to form surface intermediates, such as formates, followed by decomposition to products and desorption from the surface. The increased mobility of lattice oxygen and hydroxyl groups in copper-doped catalysts, due to an increase of the valence copper electrons as compared to iron ones, leads to an increase of conductivity and catalytic activity.

The selectivity increased due to aluminum and copper but decreased with copper alone. The definition of selectivity, used in this work, considers the number

Table 4
Catalytic activity (a), activity per area (a/Sg) and selectivity (S) of pure iron oxide (I), aluminum-doped iron oxide (IA), copper-doped iron oxide (IC), aluminum and copper-doped iron oxide (IAC) and a commercial sample at different steam to gas molar ratio (S/G) and at 370°C

Sample	$a\times 10^4$ (±0.1) (mol g^{-1} h^{-1})			$a/\mathrm{Sg}\times 10^5$ (±0.1) (mol m^{-2} h^{-1})			Selectivity (%) (±0.1)		
	$S/G=0.6$	$S/G=0.4$	$S/G=0.2$	$S/G=0.6$	$S/G=0.4$	$S/G=0.2$	$S/G=0.6$	$S/G=0.4$	$S/G=0.2$
I	7.2	5.9	5.0	9.0	6.6	5.6	49.8	49.9	19.8
IA	8.8	7.8	5.9	3.7	3.1	2.1	60.2	19.7	10.3
IC	16.2	12.9	15.0	20.2	12.9	18.7	49.6	50.1	50.4
IAC	27.0	26.4	22.2	11.7	10.5	8.3	70.2	80.0	50.8
Commercial	24.7	33.5	21.5	18.7	10.5	7.2	58.5	88.4	86.7

Table 5
Catalytic activity (a) and selectivity (S) of pure iron oxide (I sample), aluminum-doped iron oxide (IA), copper-doped iron oxide (IC), aluminum and copper-doped iron oxides (IAC) and of a commercial catalyst at different temperatures and at $S/G = 0.6$

Sample	$a \times 10^4$ (mol g^{-1} h^{-1}) (±0.1)			Selectivity (%) (±0.1)		
	350°C	370°C	400°C	350°C	370°C	400°C
I	5.2	7.2	13.2	10.1	49.8	18.6
IA	5.6	8.8	11.0	5.0	60.2	18.4
IC	13.4	16.2	20.2	52.3	49.6	87.7
IAC	24.7	27.0	27.6	84.5	70.2	66.3
Commercial	24.2	24.7	32.9	88.6	58.5	84.9

of moles of carbon dioxide produced per number of moles of carbon monoxide that reacted.

The experiments carried out at lower steam to gas ratio (Table 4) showed that the catalysts can work at $S/G = 0.4$ without any decrease to both activity and selectivity to carbon dioxide, and so does the commercial one. At $S/G = 0.2$, however, the selectivity was strongly decreased. The analysis of these catalysts showed that this behavior was likely due to the lower Fe(II)/Fe(III) ratio, which means a lower amount of the active sites.

The results of the experiments carried out at different temperatures are shown in Table 5. We can see that the activity increased with the temperature, due to kinetics factors [1] and this shows that the catalysts are stable in these conditions. On the other hand, the change of the selectivity with temperature depends on the sample suggesting that the catalysts undergo different transformations in situ. For the aluminum and copper-doped sample the selectivity decreased with the increase of temperature, probably due to hydrocarbon production from carbon monoxide. It is well known [2,3] that under low steam to gas ratio, high temperatures or high carbon monoxide concentration, metallic iron or a carbide phase may be formed. These phases can act as Fisher–Tropsch catalysts. The solids without copper (I and IA) showed very low selectivity at 350°C, a fact which can be related to their difficulty in producing the active phase in situ, in accordance with the TPR results (Fig. 2). At higher temperatures the magnetite formation was favored and an increase in selectivity was noted. With a further increase of temperature, the selectivity decreased again due to the production of hydrocarbon [2,3]. On the other hand, the copper-doped sample (IC), as well as the commercial catalyst, showed different behavior. In the first case, the selectivity changed only at 400°C while in the other it decreased and then increased with temperature. This behavior is unexpected and seems to be related with the stability of the phases in situ. However, additional experiments should be done in order to confirm it. The aluminum and copper-doped catalyst showed a higher value of selectivity at 350°C than at 370°C and close values for the activity. It means that this sample is promising to be used at lower temperatures than the industrial process (370°C) with performance similar to the commercial catalyst. However, new tests are needed to evaluate the stability of the catalysts, under the conditions close to that used in industrial operations.

The catalyst with both dopants showed an activity close to chromium and copper-doped commercial catalyst and a higher value of selectivity at 370°C. It means that it is a promising option to replace the chromium-based catalyst. The catalyst based on aluminum and copper produces the active phase more easily than the other catalysts, shows resistance to further magnetite reduction and performs well at severe conditions, that is, low steam to process gas ratio ($S/G = 0.4$) as well as at lower temperatures than the conditions used in industrial processes, leading to energy save. In addition, it can be discarded without any damage to the environment.

4. Conclusions

The addition of small amounts of copper leads to significant changes on the catalytic properties of aluminum-doped hematite. This sample easily produces the active phase, but it is resistant to further magnetite reduction. In addition, it can work at low steam to process gas ratio ($S/G = 0.4$) as well as at low temperatures, leading to energy save. This catalyst has similar catalytic properties, as compared to the chromium and copper-doped commercial one, and it can also work at energy saving conditions. However, it has the advantage of being discarded without any damage to the environment.

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