A thorium-doped catalyst for the high temperature shift reaction

João Luís Rangel Costa [a], Gustavo Sérgio Marchetti [b], Maria do Carmo Rangel [a],*

[a] *Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Federação, 40 290-170 Salvador, Bahia, Brazil*
[b] *CINDECA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900, 47 y 115 La Plata, Argentina*

Abstract

The reforming of natural gas feedstock in the presence of steam is the main industrial route to produce high purity hydrogen. However, this process also produces carbon oxides which can poison most hydrogenation catalysts as well as ammonia catalysts. In industrial processes, these compounds are often removed from the gaseous stream by the water gas shift reaction (WGSR), which is performed in two steps due to thermodynamics and kinetics considerations. A chromium and copper-doped hematite has been recently proposed as an industrial catalyst in the high temperature shift (HTS). This solid shows a stable performance but the search for non-toxic systems is much needed due to environmental restrictions related to chromium compounds. In this work, the use of thorium instead of chromium in iron- and copper-based catalysts for the HTS reaction was investigated. Catalysts were prepared in the active form (magnetite) in order to save energy, characterized by several techniques and then evaluated in operational conditions close to the industrial ones. It was found that thorium can replace chromium in these catalysts leading to better catalytic properties as compared to chromium. The catalyst has the advantage of being less toxic and can be prepared in the active phase.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Shift reaction; Thorium-doped magnetite; Hydrogen production

1. Introduction

In all ammonia plants worldwide the demand for high purity hydrogen is largely met by reforming natural gas feedstock in the presence of steam. However, this process produces carbon oxides which may irreversibly deactivate the ammonia catalyst. That requires another industrial unit, in which carbon monoxide is oxidized to carbon dioxide in a water gas shift reaction (WGSR), with the product being removed by sodium carbonate in a scrubber. The synthesis gas produced is purified by methanation of the residual carbon monoxide and dioxide [1,2]. Besides these reactions, the production of the synthesis gas involves a preliminary step of desulfurization since the sulfur compounds, usually

present in the feedstock, may poison the reforming catalyst as well as the WGSR ones [1].

The WGSR [2]
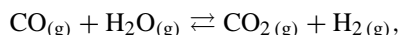
$$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2\,(g)} + H_{2\,(g)},$$
$$\Delta H = -40.6\,\text{kJ mol}^{-1}$$

is favored by low temperatures and excess of steam due to its reversibility and exothermicity. However, it takes high temperatures to achieve rates for industrial applications. As a consequence, this reaction is often carried out in two steps, the first being performed at in range 320–450 °C (named high temperature shift—HTS) whereas, in the other one, carbon monoxide is removed in thermodynamically favorable conditions at 200–250 °C (low temperature shift—LTS) [2].

Most industrial HTS catalysts contain iron oxide, as well as chromium oxide, which is believed to act

---

* Corresponding author.

as a stabilizer retarding sintering and loss of surface area [1–3]. These catalysts are often commercialized as hematite (α-Fe_2O_3) and are reduced in situ to produce magnetite (Fe_3O_4) which is found to be the active phase [3]. This reaction is highly exothermic and should be controlled to avoid the production of metallic iron, which may catalyze undesirable reactions such as Fischer–Tropsch synthesis [1]. In industrial processes, large amounts of steam are used to inhibit the metallic iron formation. However, this implies high operational costs and the development of catalysts in the active phase is much needed.

The chromium- and iron-based catalysts have been used in commercial processes for more than 60 years and show high stability and performance. In recent times, these solids have been improved by adding small amounts of copper, resulting in more active and selective catalysts [4,5]. They have already been used in industrial plants and are able to work in more severe conditions, e.g. lower steam to carbon ratios without being reduced to metallic iron. These systems offer a more operating flexibility as compared to the classic HTS catalysts, since the highest activity allows the use of smaller bed volume without affecting the plant performance. Besides, the protection against metallic iron formation, and hence the hydrocarbons production, saves hydrogen and requires lower operating temperatures reducing catalysts sintering rates to ensure long life.

However, due to the environmental restrictions concerning the discarding of chromium compounds, the search for less toxic catalysts, that can be easily handled and discarded, is much needed.

Considering these aspects, this work deals with the replacement of chromium by thorium in HTS catalysts. In order to save the energy related to the steam consumption, the catalysts were prepared in the active phase (magnetite).

2. Experimental

2.1. Catalyst preparation

All reagents used were of analytical grade. The catalysts were prepared by precipitation techniques followed by heating at 500 °C for 2 h under nitrogen flow (100 ml min^{-1}). Four kinds of samples were prepared:

(i) with thorium and copper (TC sample); (ii) with thorium (T); (iii) with copper (C) and (iv) without any dopant (M). The iron to the dopant molar ratio was kept the same in all cases (Fe/Th, Cu = 10) in a value close to that of chromium in commercial formulations.

The thorium- and copper-based catalyst was prepared by adding, under stirring, aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ (1 M) and $Th(NO_3)_4 \cdot 9H_2O$ (0.1 M) 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 as well as to remove the ammonium hydroxide. The supernatant was analyzed for nitrate ions and the gel was washed and centrifuged again. After a second centrifugation step, the gel was impregnated with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.01 M) for 24 h under stirring. This method intends to avoid that copper could be complexed by ammonium ions [6]. The sol obtained was then centrifuged and rinsed four times with a 5% (w/v) ammonium acetate solution to promote the sorption of acetate ions [7–9] on the gel, 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 supernatant after each centrifugation. The formation of $[Fe(NO)]^{2+}$ was detected by a brown ring [10]. The metal contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES) by using an Arl 3410 model machine.

The sorption of acetate ions on the precursors of the catalysts was confirmed by Fourier transformer infrared spectroscopy in the range 4000–400 cm^{-1} using a model Valor II Jasco spectrometer and KBr discs.

X-ray diffractograms were recorded at room temperature with a model D-5000 Siemens equipment using Cu Kα radiation generated at 40 kV and 40 mA in the range of $2\theta = 10$–$90°$. 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.

The Mössbauer spectra were obtained in transmission geometry, with a 512-channel constant acceleration spectrometer at room temperature. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 μm thick α-Fe foil. All isomer shifts mentioned in this paper are referred to this standard at 298 K. The spectra were evaluated by using a least-squares nonlinear computer fitting program with constraints. Lorentzian lines were considered with equal widths for each spectrum component. The spectra were folded to minimize the geometric effects.

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 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, 50% H_2 and 30% 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 a steam to gas molar ratio of 0.6 (0.38% mole of water in the feed) and 370 °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. In order to state the role of thorium and copper in these catalysts mechanical mixtures made off magnetite and copper oxide (MCM sample), magnetite

and thorium oxide (MTM sample) and magnetite, thorium oxide and copper oxide (MCTM) were also evaluated in the reaction. These tests were carried out at 200 °C because of the tendency of copper to sinter [2].

3. Results and discussion

The contents of iron, thorium and copper are shown in Table 1. One can see that in all samples the experimental Fe/Cu and Fe/Th ratios are close to the initial ratios. It means that the experimental conditions promoted the simultaneous precipitation of iron and thorium compounds, since they precipitate in the same pH range and have similar hydrolysis constants [11]. Copper was mostly sorbed on the gel rather than complexed by the residual ammonium ions as noted in other works [12]. This fact suggests that adsorption forces stronger than complexion forces were generated in the gel. By rinsing the gel with an ammonium acetate solution, the acetate ions substituted some hydroxyls groups in the structure producing an iron and thorium hydroxyacetate, which was able to produce magnetite in the calcination step [7]. It can also be noted that the sorption of copper on the iron particles was not affected by the presence of thorium.

The infrared spectra of the precursors of the catalysts are shown in Fig. 1. The presence of acetate in the solids was confirmed by the absorption bands at 1558 and 1430 cm^{-1}, due to the asymmetric and symmetric stretching modes, respectively [13]. The spectra also show a narrow band at 1385 cm^{-1} due to nitrate groups [14]. The broad band at 3392 cm^{-1} was assigned to the stretching mode of the hydroxyl groups in the adsorbed water [14]. The absorption band noted in the range 800–400 cm^{-1} was attributed to the Fe–O stretching mode in iron hydroxide and the band at

Table 1
Elemental analysis results of pure iron oxide (M sample), copper-doped iron oxide (C), thorium-doped iron oxide (T) and thorium- and copper-doped iron oxide (TC)

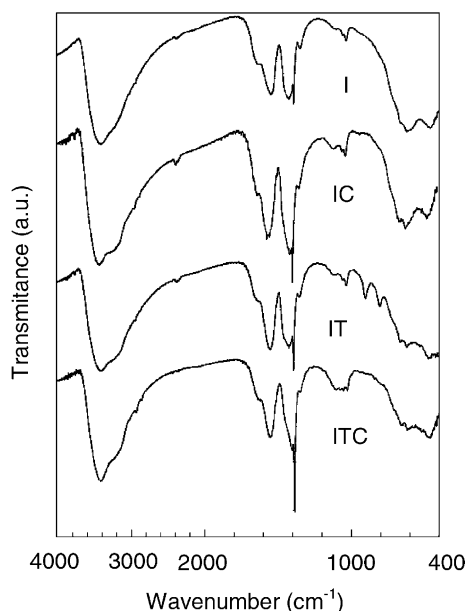| Sample	% Fe (±0.05)	% Th (±0.03)	% Cu (±0.03)	Fe/Th (molar) (±0.1)	Fe/Cu (molar) (±0.1)
M	68.90	–	–	–	–
C	89.95	–	10.05	–	10.2
T	67.38	32.62	–	8.6	–
TC	62.45	30.68	6.87	8.4	10.3

Fig. 1. Infrared spectra of the precursors of the catalysts. I sample: pure iron (hydr)oxide; IC and IT: copper- and thorium-doped sample, respectively, and ITC: thorium- and copper-doped sample.

Table 2
Surface area (S_g) of pure iron oxide (M sample), copper-doped iron oxide (C), thorium-doped iron oxide (T) and thorium- and copper-doped iron oxide (TC) and of a commercial catalyst before and after the catalytic tests at steam to gas molar ratio (S/G) of 0.6 at 370 °C

Sample	S_g (m^2 g^{-1}) (fresh catalysts)	S_g (m^2 g^{-1}) (spent catalysts)
M	18	10
C	16	10
T	35	32
TC	32	26
Commercial	58	13

$1026 \, cm^{-1}$ is characteristic of the deformation mode of OH groups on the surface of iron hydroxide [15].

Magnetite was found in the fresh catalysts (Fig. 2), in accordance with previous works [7–9]. Thorium oxide was also detected. As Cu^{2+} species have an ionic

radius (0.73 Å) similar to the Fe^{2+} species (0.74 Å), they are expected to go into the magnetite lattice occupying the octahedral sites [16] rather than to segregate as another phase. Because of the similarity of the size of the ions, Cu^{2+} species should not cause any stress in the magnetite lattice and then no change of the cell parameter is expected. On the other hand, thorium should cause an expansion of the cell parameter due to the ionic radius of the Th^{4+} species (0.94 Å). In the present work, no change in the cell parameter was noted and then one can conclude that thorium went to the surface or segregated as another phase. The spent catalysts showed similar pattern of X-ray diffraction.

The surface area of the fresh and spent catalyst are shown in Table 2. The presence of either thorium or the two dopants increased the surface area of the fresh catalysts, conversely doping the solid with copper alone did not affect the surface area. This can be explained by considering that Cu^{2+} ions tend to distribute uniformly in the structure [16] and their introduction in the lattice does not cause stress. If some stress is generated in the solid, the equilibrium particle size is shifted toward smaller particles since the ratio of strain to the surface effects becomes greater for larger particles [17]. On the other hand, thorium is too big to go into the magnetite lattice and its action can be associated with a surface phenomenon in which it keeps the particles apart from each other, in accordance with previous works carried out with iron-based catalysts [18]. The same tendency was noted for the used catalysts. These results means that the thorium presence produced smaller iron oxides particles (in accordance with the broadening of the DRX lines) and avoided the sintering of these solids. The test reaction strongly decreased
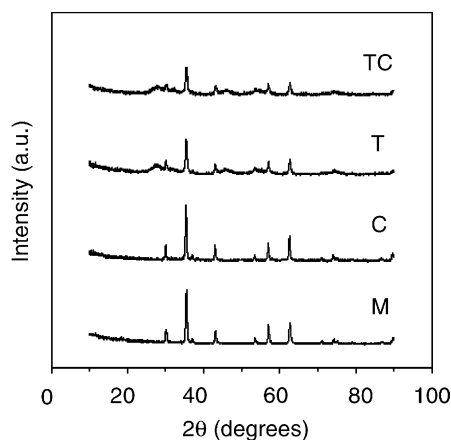

Fig. 2. X-ray diffractograms of fresh catalysts. M sample: pure iron oxide; C and T: copper- and thorium-doped sample, respectively, and TC: thorium- and copper-doped sample.

the surface area except in the sample with thorium alone. This can be assigned to the presence of steam which favors sintering in accordance with other works [4]. The commercial catalyst showed a similar behavior. The surface area of the solids are lower than the traditional chromium-doped catalysts reported by several authors [2,3] as 70–100 $m^2 g^{-1}$. However, the commercial copper and chromium-based catalyst shows a lower area, as shown in Table 2. This can be assigned to the copper as we had concluded in a previous work [9]. After the catalytic tests, the thorium-doped samples showed areas higher than the commercial catalyst.

The TPR curve of the fresh magnetite (Fig. 3) showed one peak at 350 °C, due to reduction of Fe^{3+} to Fe^{2+} species, and a broad peak in the range 400–780 °C attributed to the formation of metallic iron [19]. The last peak has a shoulder probably due to the iron reduction in the outer layers of the particles in a first step. The copper-doped catalyst showed a TPR curve with a peak at 220 °C, assigned to metallic copper [20] and another one in the range 400–800 °C due to metallic iron. The peak attributed to the reduction of Fe^{3+} to Fe^{2+} disappeared and that due to metallic iron began at around 350 °C. It suggests that the high

temperature peak is related to both processes. Its maximum was shifted to lower temperatures, as compared to pure iron oxide, showing that copper makes the production of metallic iron easier. In the thorium-doped sample, the first peak was shifted to lower temperatures (250 °C), whereas the other one was displaced to higher temperatures (400–1000 °C); this behavior shows that this metal eases the production of Fe^{2+} species but makes the metallic iron formation more difficult and thus increases the stability of the active phase. The thorium- and copper-doped solid showed a curve with the characteristic peak due to metallic iron formation displaced to higher temperatures, showing that both dopants make the production of metallic iron more difficult. Comparing this curve with the sample with copper alone, one can see that thorium shifted the peak due to the production of metallic copper to lower temperatures (200 °C), showing that this dopant favors this process. The high temperature peak is displaced, suggesting that the dopants make the production of metallic iron more difficult. These results showed that copper favors the production of metallic iron while thorium makes this process more difficult.

All catalysts were active to HTS reaction as shown in Table 3. 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. Copper increased the activity of magnetite and the activity per area which suggests an electronic effect of this dopant. Although copper is also active to the shift reaction, the high temperature (370 °C) of the HTS step may lead to sintering and thus copper would cause only a light increase in the activity. In addition, most of copper is expected to be in the bulk of solid [16].
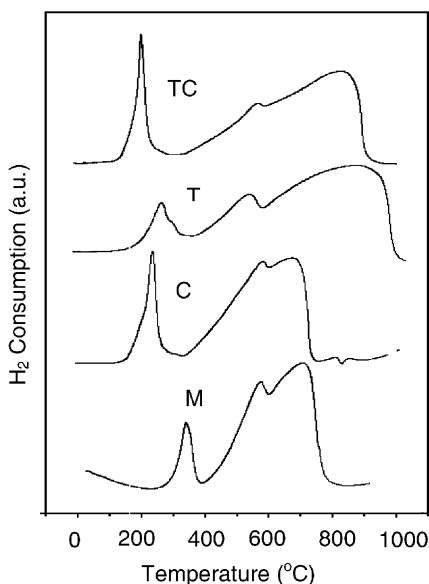

Fig. 3. TPR curve of fresh catalysts. M sample: pure iron oxide; C and T: copper- and thorium-doped sample, respectively, and TC: thorium- and copper-doped sample.

Table 3
Catalytic activity (a), activity per area (a/S_g) and selectivity towards CO_2 yield (S) of pure iron oxide (M), copper-doped iron oxide (C), thorium-doped iron oxide (T), thorium- and copper-doped iron oxide (TC) and a commercial sample at a steam to gas molar ratio of 0.6 at 370 °C

Sample	$a \times 10^4$ (± 0.1) ($mol\,g^{-1}\,h^{-1}$)	$a/S_g \times 10^5$ (± 0.1) ($mol\,m^{-2}\,h^{-1}$)	Selectivity (± 0.1) (%)
M	8.8	8.8	83.1
C	16.1	16.1	82.2
T	9.2	2.9	84.0
TC	28.9	11.0	85.3
Commercial	24.7	18.7	58.5

Table 4
Catalytic activity (*a*) of copper-doped iron oxide (C), thorium-doped iron oxide (T), thorium- and copper-doped iron oxide (TC) and of mixtures of magnetite and copper oxide (MCM), magnetite and thorium oxide (MTM) and magnetite, thorium oxide and copper oxide (MCTM) at a steam to gas molar ratio of 0.6 at 200 °C

Sample	$a \times 10^4$ (±0.1) (mol g^{-1} h^{-1})
C	6.9
MCM	3.8
T	3.2
MTM	2.2
TC	8.5
MTCM	2.9

Fig. 4. Activity of the catalysts in HTS reaction as a function of time. (◆) M sample, (■) C sample, (▲) T sample, (×) TC sample.

The high increase observed in the performance of the catalysts suggests that copper itself has not a significant role as an active site but rather as a promoter. These conclusions were confirmed by measuring the activity of a mechanical mixture of copper oxide and magnetite. As shown in Table 4, the M sample is more active than the mixture (MCM) probably due to an electronic effect of copper. On the other hand, thorium decreased the activity per area and increased the surface area; these effects compensated each other resulting in a catalyst with an activity close to pure magnetite. Therefore, this dopant causes an electronic effect on magnetite which damages the active sites. This was confirmed by comparing the activity of the thorium-doped sample (T) with a mechanical mixture of thorium and magnetite (Table 4). As we can see, the activity of the last one (MTM) is close to that of the T sample. In the first case (MCM), there is no thorium to
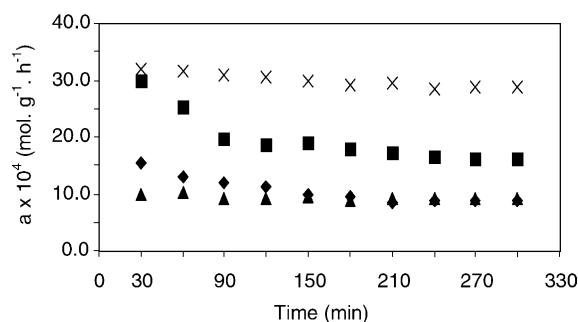
damage the active sites or to increase the surface area. In the other one (T), the damage of the active sites is partially compensated by the increase of surface area. The simultaneous presence of both thorium and copper increased even more the activity of magnetite and this value (28.9×10^{-4} mol g^{-1} h^{-1}) was higher than a commercial chromium- and copper-based catalyst (24.7×10^{-4} mol g^{-1} h^{-1}). Comparing this sample with a mechanical mixture of magnetite, thorium oxide and copper oxide (Table 4) we see that the last catalyst was less active which suggests that the action of copper is more important than the surface area in increasing the activity of magnetite.

Fig. 4 shows the activity of the catalysts as a function of time. It can be seen that all catalysts slowly deactivated with time and this effect was more intense in the sample doped with copper alone. This behavior seems to be related to the loss of surface area due

Table 5
Mössbauer parameters of pure iron oxide (M), copper-doped iron oxide (C), thorium-doped iron oxide (T) and thorium- and copper-doped iron oxide (TC) before the test reaction

| Species	Parameters[a]	M	C	T	TC
Fe$_3$O$_4$, A site (tetrahedral)	H_A (T)	49.55 ± 0.02	49.72 ± 0.03	49.41 ± 0.04	49.17 ± 0.06
	δ_A (mm s^{-1})	0.32 ± 0.01	0.31 ± 0.01	0.31 ± 0.01	0.30 ± 0.01
	$2\varepsilon_A$ (mm s^{-1})	−0.01 ± 0.01	−0.03 ± 0.01	−0.03 ± 0.01	−0.04 ± 0.02
Fe$_3$O$_4$, B site (octahedral)	H_B (T)	45.86 ± 0.06	46.21 ± 0.06	45.7 ± 0.1	45.6 ± 0.1
	δ_B (mm s^{-1})	0.64 ± 0.01	0.64 ± 0.01	0.60 ± 0.01	0.59 ± 0.01
	$2\varepsilon_B$ (mm s^{-1})	0.03 ± 0.01	−0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02
	B/A ratio	0.46	0.70	1.02	1.90
	x	0.18 ± 0.01	0.13 ± 0.01	0.08 ± 0.02	−0.01 ± 0.02
	Fe$_{3-x}$O$_4$	Fe$_{2.82}$O$_4$	Fe$_{2.87}$O$_4$	Fe$_{2.92}$O$_4$	Fe$_{3.01}$O$_4$

[a] All isomer shifts are referred to α-Fe at 298 K.
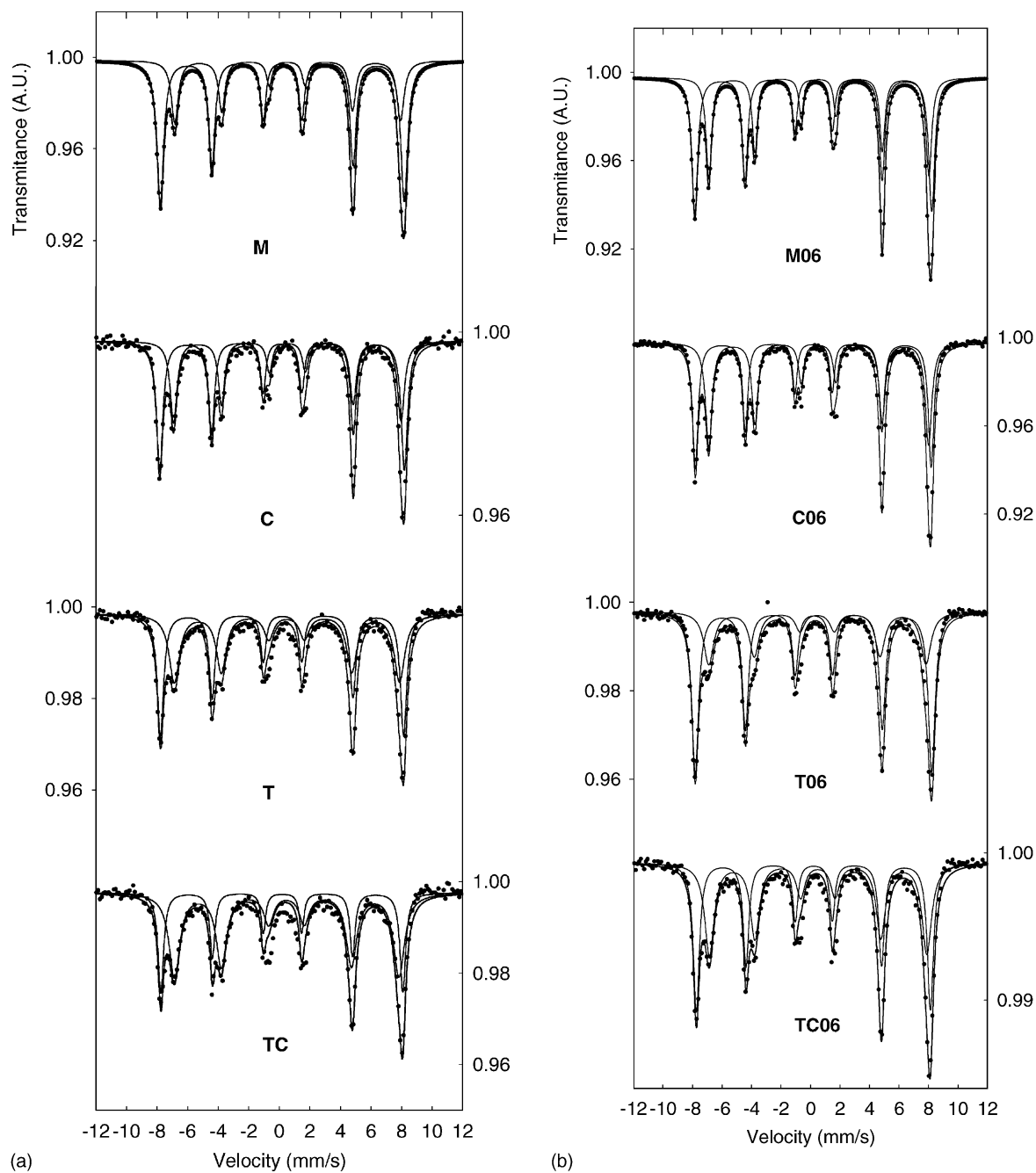
Fig. 5. Mössbauer spectra of (a) fresh and (b) spent catalysts. M sample: pure iron oxide; C and T: copper- and thorium-doped sample, respectively, and TC: thorium- and copper-doped sample.

to the reaction. It can also be noted that the most stable catalysts were the thorium-doped ones, the solids which kept the surface area during reaction.

The selectivity of the catalysts were not affected due to the dopants and the values were close to the commercial sample. The definition of selectivity, used in this work, considers the number of moles of carbon dioxide produced per number of moles of carbon monoxide that reacted.

The increased activity of the copper-doped catalysts can be explained by the two mechanisms discussed in the literature. In the regenerative mechanism [21], the surface undergoes successive oxidation and reduction cycles by water and carbon monoxide, respectively, to form the corresponding hydrogen and carbon dioxide products. The conditions for these cycles are more favorable in the copper-doped solids, as shown by the TPR results, from which we can see that copper favors the Fe^{2+} production. In the adsorptive mechanism [22], 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 in the electron density as compared to pure iron oxide, leads to an increase of conductivity and catalytic activity. In the case, lattice oxygen reacts with carbon monoxide to produce carbon dioxide and, in a further step, lattice oxygen is regenerated by steam to produce hydrogen [22].

The Mössbauer spectra of the fresh and used catalysts are shown in Fig. 5 and the Mössbauer parameter are shown in Tables 5 and 6. These results confirmed
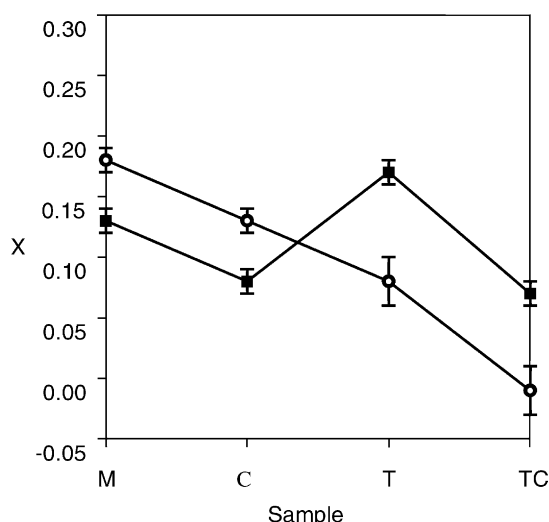

Fig. 6. Oxidation parameter of the fresh and used catalysts calculated by the Mössbauer spectra. M sample: pure iron oxide; C and T: copper- and thorium-doped sample, respectively, and TC: thorium- and copper-doped sample. (○) Fresh catalyst and (■) spent catalyst.

that magnetite was the only iron-based phase in accordance with X-ray diffractograms. The presence of the dopants changed the oxidation degree of the samples in the order M > C > T > TC in the fresh catalysts as shown in Fig. 6. In this case, X is the oxidation parameter in magnetite with a formula of $Fe_{3-x}O_4$ and then as higher is X, more oxidized magnetite is. This parameter was calculated from the following expression: $X = (2 - 1.1R)/(6 + 4.945R)$ where R is the area ratio of the Mössbauer signals belonging to the

Table 6
Mössbauer parameters of pure iron oxide (M), copper-doped iron oxide (C), thorium-doped iron oxide (T) and thorium- and copper-doped iron oxide (TC) after the test reaction

Species	Parameters[a]	M	C	T	TC
Fe_3O_4, A site (tetrahedral)	H_A (T)	49.89 ± 0.02	49.67 ± 0.02	49.80 ± 0.03	49.30 ± 0.04
	δ_A (mm s^{-1})	0.30 ± 0.01	0.30 ± 0.01	0.32 ± 0.01	0.31 ± 0.01
	$2\varepsilon_A$ (mm s^{-1})	-0.02 ± 0.01	-0.02 ± 0.01	-0.03 ± 0.01	-0.03 ± 0.01
Fe_3O_4, B site (octahedral)	H_B (T)	46.36 ± 0.03	46.29 ± 0.03	45.7 ± 0.1	45.78 ± 0.09
	δ_B (mm s^{-1})	0.66 ± 0.01	0.65 ± 0.01	0.56 ± 0.01	0.61 ± 0.01
	$2\varepsilon_B$ (mm s^{-1})	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.03	0.02 ± 0.02
	B/A ratio	0.68	1.01	0.52	1.05
	x	0.13 ± 0.01	0.08 ± 0.01	0.17 ± 0.01	0.07 ± 0.01
	$Fe_{3-x}O_4$	$Fe_{2.87}O_4$	$Fe_{2.92}O_4$	$Fe_{2.83}O_4$	$Fe_{2.93}O_4$

[a] All isomer shifts are referred to α-Fe at 298 K.

two iron sites [23]. After the reaction, the M and C samples were more reduced and thus more stoichiometric. The C sample is more stoichiometric than the M sample and it explains its higher intrinsic activity [2]. On the other hand, the thorium-doped samples were less stoichiometric probably due to its action in making the Fe^{3+} reduction more difficult, as shown by TPR. This result can explain the action of this dopant in damaging some active sites. The TC sample showed an oxidation degree close to the C sample, which justifies the similar values of intrinsic activity. The high activity of the TC sample is also due to the increase of surface area by thorium.

These results showed that the thorium- and copper-doped magnetite is a promising option to replace the chromium- and copper-doped catalyst. This sample is produced in the active phase leading to energy save, shows resistance to further magnetite reduction and performs well in the conditions used in industrial processes. In addition, it can be discarded without any damage to the environment.

4. Conclusions

Thorium- and copper-doped magnetite is an efficient catalyst to HTS reaction. In these solids copper acts as a structural promoter whereas thorium prevents sintering and the production of metallic iron which can catalyze undesirable reactions. However, thorium damages some active sites and decreases the activity per area. The most active catalyst is obtained when both thorium and copper are present in the solid. It is more active and selective than a chromium- and copper-doped commercial catalyst. Therefore, this catalyst is promising for industrial applications, since it shows several important features like be non-toxic, in comparison to the high chromium toxicity, have better performance as compared to the chromium-doped ones and can be prepared in the active phase reducing the energy consumption.

References

[1] L. Lloyd, D.E. Ridler, M.V. Twigg, in: M.V. Twigg (Ed.), Catalysis Handbook, Wolfe Scientific Books, London, 1996, 339 pp.
[2] D.S. Newsome, Catal. Rev.-Sci. Eng. 21 (1980) 275.
[3] H. Bohlbro, Investigation on Kinetics of the Conversion of Carbon Monoxide with Water Vapour over Iron Oxide Based Catalysts, 2nd ed., Haldor Topsoe Research Laboratory, Copenhagen, 1969, 6 pp.
[4] G.C. Araújo, M.C. Rangel, Catal. Today 62 (2000) 201.
[5] G.C. Araújo, M.C. Rangel, in: A. Corma, F.V. Melo, S. Mendioroz, J.L. Fierro (Eds.), Studies in Surface Science and Catalysis, vol. 130, Elsevier, Amsterdam, 2000, 1601 pp.
[6] F. Basolo, R. Johnson, Química de los Compuestos de la Coordinación, Editorial Reverté, SA, Barcelona, 1980, pp. 84, 144.
[7] M.C. Rangel, F. Galembeck, J. Catal. 145 (1994) 364.
[8] M.C. Rangel, R.M. Sassaki, F. Galembeck, Catal. Lett. 33 (1995) 237.
[9] E.B. Quadro, M.L.R.M. Dias, A.A.M. Amorim, M.C. Rangel, J. Braz. Chem. Soc. 10 (1999) 51.
[10] A.I. Vogel, Macro and Semimicro Qualitative Inorganic Analysis, Longmans, Buenos Aires, 1953, 338 pp.
[11] J. Burguess, Metal Ions in Solution, Wiley, New York, 1978, 269 pp.
[12] M.O.G. Souza, E.B. Quadro, M.C. Rangel, Química Nova 21 (1998) 428.
[13] R. Silverstein, G.C. Basslerand, T.C. Morrill, Spectrometry Identification of Organic Compounds, Wiley, New York, 1968, 121 pp.
[14] R.A. Niquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, Orlando, 1971, 3 pp.
[15] J.D. Russel, Clay Miner. 14 (1979) 109.
[16] P.S. Sidhu, R.J. Gilkes, M. Posner, J. Inorg. Nucl. Chem. 40 (1978) 429.
[17] H. Topsoe, J.A. Dumesic, M. Boudart, J. Catal. 28 (1978) 477.
[18] A. Nielsen, H. Bohlbro, An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia, Gjellerup Forlag, Copenhagen, 1968, 221 pp.
[19] J.C. Gonzalez, M.G. González, M.A. Laborde, N. Moreno, Appl. Catal. 20 (1986) 3.
[20] S. Pinna, T. Fantinel, G. Strukul, A. Benedetti, N. Pernicone, Appl. Catal. 49 (1997) 341.
[21] G.K. Boreskov, T.M. Yureva, A.S. Sergeeva, Kinet. Katal. 11 (1970) 1476.
[22] W.F. Podolski, Y.G. Kim, Ind. Eng. Chem. Process., Des. Dev. 13 (1974) 415.
[23] A.M. van der Kraan, Phys. Status Solidi (a) 18 (1973) 215.