

Zr-supported CuFe_2O_4 nanoparticles as catalysts for the combustion of propane

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ABSTRACT

The nanoparticles of CuFe_2O_4 , with spinel structure, supported over ZrO_2 and sulphated ZrO_2 , have been obtained by wet chemical synthesis, through the precursor citrate route. The supported catalysts, containing a ferrite/support ratio up to 30%, were thermally treated within the range 150 to 700°C, and characterized by XRD, TPR, FTIR, SEM-EDX, TEM and Mössbauer spectroscopy. The propane combustion was performed as a reaction test.

In the family of Zr-supported CuFe_2O_4 catalysts investigated, the catalytic activity is dependent of the temperature of activation and the characteristics of the Zr-support. Indeed, the thermal treatment promotes the growth of the size and **crystal degree of** **(?? Puede ser size and degree of crystallinity of)** the Cu-ferrite particles supported over ZrO_2 , a reduction in the BET surface and reducibility which explain the decline in the activity as the temperature of annealing increases, as a general trend.

In the case of SZr supported samples a change in the structure of the support, due to desulphation, around 600°C seems to influence the catalytic activity causing a sharp decrease in the conversion of propane, due to a significant change in morphology and redox behaviour when the material is annealed at 700°C.

Nevertheless, despite the differences in the physical-chemical characteristics of the Zr supports, both Zr-supported CuFe_2O_4 catalysts treated at 400°C, behave as active catalysts for propane combustion of similar efficiency.

1. Introduction

Most of the technologies based on hydrocarbon combustion (HC) as fuels lead to the release in the environment of both gas and particulates, such as CO , NO_x and

unburnt HC. These pollutants have primary and secondary impacts on air quality, human health and climate. Furthermore NO_x and soot particulate emitted from diesel exhaust have been causing severe environmental and health problems [1].

The air pollution control is a pressing need in both industrialized and developing nations. In this way the regulations include more strict limits to gas emissions. At the same time through the last 30 years of research and development, significant reduction in CO, NO_x, and HC have been achieved through the catalytic combustion process [2].

Liquefied Petroleum Gas (LPG) has been extensively applied in the fuel-powered vehicles because of its attractive features, such as clean combustion, high energy-density, simple storage and ready for use in transportation [1].

The exhaust gas from LPG combustor (e.g. LPG Engines and burners) still contains a significant amount of hydrocarbons, which are hazardous to the environment and contribute to atmospheric greenhouse gas effects [3,4]. The primary source of emitted hydrocarbons from LPG burners or engines are low-carbon organic compounds in which propane is the most abundant and is rather difficult to eliminate [4].

Catalytic combustion represents a promising and low-cost technology for both energy efficacy and control of organic pollutant emissions, however, such techniques are highly dependent on the effectiveness of the combustion catalyst [4-8]. In order to meet the even tighter environmental legislations, it has become necessary to develop efficient catalysts for catalytic combustion of the emitted propane from LPG combustors [4,8]. In addition, the suitable catalysts are also highly desired for the propane-fueled solid oxide fuel cells since they share the same requirements []

The catalytic combustion technology was available since the 70th, but the commercial application was imminent more recently due to the development of stable catalysts and to the introduction of new engineering approaches [3].

~~This is an effective alternative to reduce significantly the temperature at which most fossil fuels burn, in general, and natural gas (or liquefied) particularly (es correcta esta frase, no me suena creo que falta algo).~~ The presence of a catalyst allows the control of the adverse conditions of the homogeneous process. In catalytically assisted combustion it is possible to operate gas turbines with lower gas mixtures and higher efficiency. In addition the main advantage of this process, over the conventional thermal

combustion, is the drastic decrease of NO_x formation. The hybrid combustion system, which consists of a combination of catalytic and homogeneous combustion, seems a viable design [4].

The catalytic system used in propane combustion generally consists of an active component and a support or substrate. The noble metals (Pd, Pt, Rh and Au), which are subjected to deactivation due to sintering and catalyst poison [4,11], and many oxides, such as simple and mixed oxides, spinels, perovskite, etc., are involved in catalytic combustion of lower alkanes [5-8].

In the last years, research has been carried out on transition metals mixed oxides, of the general formula A^{II}B^{III}₂O₄ with spinel type structure spinel type (error), particularly the ferrites MFe₂O₄, which are active and thermally more stable. On the other hand there is a great availability of the raw materials necessary for the synthesis of these materials. Moreover the main advantage of metallic oxide catalysts is their low cost compared to those of noble metals. These oxides have been studied for a great variety of applications, including catalysis. Some of them have proved to catalyze efficiently CO to CO₂ [9-11] oxidation, the combustion of organic compounds [12,13], the reduction of NO_x by hydrocarbons or particulate material [14,15], the methane reforming [16], and catalytic hydrogen production [17] (porque está resaltado??). According to these studies, the oxides containing Cu, Co, Fe and Cr are potentially interesting for the catalytic combustion of hydrocarbons since these have a relatively high activity and an acceptable stability.

Recently a cobalt spinel catalyst, obtained by citrate-precursor synthesis, exhibited for catalytic combustion of propane at (no esta de más) a very low reaction temperature [18]. It(no esta de más) is in this context that it was suggested that the defects of the spinel lattice play a key role due to the generation of electrophilic O⁻ species which are crucial for the catalytic oxidation of hydrocarbons.

On the other hand in a previous work of samples of bulk CuFe₂O₄ was applied as catalysts for hydrocarbon (HC) oxidation [19]. In this work it was demonstrated that the chemical synthesis and calcinations temperature have influence on the relevant physical chemical properties for the catalytic activity.

The catalytic combustion process of many mixed metal oxides over many conventional supports has been extensively studied [20 agregar citas]. The materials supported over ZrO₂ have been investigated in order to increase the surface area with the aim to enhance the activity (?). In this way, transition metal doped-ZrO₂

(cubic) catalysts have been investigated for the combustion of dilute propane [21]. The effect of the structure and morphological properties on the catalytic activity of sulphate doped-ZrO₂ systems has also been analyzed [22]

It is in this context that, the purpose of this work is to analyze the influence of the support on the catalytic behaviour CuFe₂O₄ for dilute propane combustion using ZrO₂ and sulphated ZrO₂. The materials were obtained from precursors, through the as-called citrate route and fully characterized by different techniques, after each thermal step, with aim to correlate the structure, morphology, surface and reducibility with the catalytic activity exhibited.

2. Experimental

2.1 Catalysts preparation

A wet chemical method allows the preparation of a powder with greater homogeneity and smaller size particles because departing from aqueous solutions allows the atomic mixing of the elements involved in the mixed oxide formation over the ceramic support. For this reason the CuFe₂O₄ supported catalysts were prepared using the method of the citrate complexation of the metals. According to this chemical synthesis the aqueous solutions, containing stoichiometric amounts of Cu(NO₃)₂·3H₂O (Riedel-de Haën) and Fe(NO₃)₃·9H₂O (Malinckrodt), were prepared and then mixed with aqueous citric (marca?? Es mejor) acid into a homogenous solution. One equivalent of citric acid was used to each total equivalent mole of the metals, in order to obtain the chelate complex with the purpose to prepare the supported CuFe₂O₄ materials. This solution was mixed with the adequate amount of the two Zr-supports, under vigorous stirring. ZrO₂ oxide (Z-TECH Corporation) and ZrO₂((OH)₂SO₃)_m·nH₂O (XZO 1249, Mel Chemical Co) were employed as Zr-supports. The resulting suspension was concentrated by heating with constant stirring until viscous brown slurry was (no está de más) obtained at 70°C. The slurry was dehydrated at about 80 °C in a sand bath for 2 h and the product was finally dried under vacuum at 95°C. During this thermal treatment the volume of the gel increases markedly showing big pores and a puffy appearance. The resulting solid was ground and submitted to the following thermal schedule by heating in a furnace: 4 h at 150°C, 4 h at 400°C and finally 4 h at 700°C, with intermediate grindings.

The catalysts were labelled as CiX-Y-T, where X corresponds to the Zr-supports, i.e: ZrO₂ (Zr) or Sulphated ZrO₂ (ZS), the numbers Y indicate the ferrite percentage and

T the temperature at which they were treated, respectively. In order to analyze the influence of the metal loading, the catalytic activity of several catalysts, prepared with ferrite/support ratio 10, 20 and 30% were evaluated. The material containing 30% load showed the best performance and therefore it was selected to carry out the study.

2.2 Samples characterization

The samples were characterized by N₂ adsorption, Thermal Analysis, X-Ray Diffraction, FTIR, Mössbauer Spectroscopy and Temperature Programmed Reduction .

The analysis by **DRX** XRD was carried out in a Philips PW 3710 diffractometer with Cu anode and graphite monochromator. FTIR spectra were measured through Magna 550 equipment, Nicolet, with Csl optics, applying “pellets” technique of KBr.

The catalyst precursors were submitted to thermal analysis, using a Shimadzu TGA-50 instrument. The heating treatment was performed at 10°Cmin⁻¹, up to 700°C, in an air flow of 40 cm³min⁻¹.

Textural parameters, specific surface and pore volume were determined by nitrogen absorption at 77K, in an Accusorb 2100E Micrometrics equipment. The data was interpreted using the BET equation.

The morphology of the samples was analyzed in a Philips, model SEM 550 with EDAX analyzer. An Au film was deposited on the samples to achieve a good resolution in the obtained images. The mean particles sizes were estimated from TEM observations, carried out on a JEOL 100CX microscope.

The Mössbauer spectra recorded at room temperature were obtained in a spectrometer with transmission geometry of 512 channels, with constant acceleration. A P57PCo source in Rh matrix of 50 nominal mCi was used. The speed calibration was carried out using α-Fe sheet of 12 μm thick. All isomeric shifts (δ) mentioned in this paper are referred to that standard. Mössbauer spectra were evaluated by means of a commercial adjusting program called Recoil, using Lorentzian lines. All spectra were doubled for minimizing geometric effects.

The active species were determined by TPR in a conventional flow reactor, fed with 20 ml/min of a N₂:H₂ = 9:1 mixture for a solid sample of 30 mg. The temperature varied between 100 and 800°C at a rate of 10 °C min⁻¹.

2.3 Catalytic measurements

The catalytic performance was carried out in a fixed bed flow reactor containing 0.12 g of catalyst, a total flow of 100 cm³/min, in a temperature range from 200°C to total conversion at a temperature rate of 1°C.min⁻¹. The feed gas contains 1000 ppm propane, 1000ppm NO, 4% O₂ and He as balance. The reactor feeding and effluent were analyzed by means of an “on line” Shimadzu GC-8A chromatograph using a CTR1 column (Alltech) at 40°C, on thermal conductivity detector. Propane combustion was studied by determining the hydrocarbon conversion as a function of temperature (light-off curves)

3. Results and discussion

3.1 Structural characterization of the support, by XRD and FTIR analysis

Firstly the full characterization of the supports, commercially available as raw materials, was carried out. According to the chemical analysis of ZrO₂, the main impurity of 1.9% is HfO₂, which is normally present in this mineral due to the extremely difficult separation of Zr from Hf. The reason for this is the well known similarity between the crystal chemistry of Zr(IV) and Hf(IV) which ionic radii are identical [23]. A low amount of 0.9% of SiO₂ is also present and the amounts of the rest of the elements are negligible.

The XRD patterns, shown in Fig 1a, indicate that all the peaks belonging to the monoclinic ZrO₂ structural modification (JCPDF N°: 37-1484), which is stable at ambient temperature, are present [22]. The peak at 2θ: 26.9° confirms the presence of a small amount of SiO₂, as highly crystalline quartz (JCPDF N°: 38-0360). The presence of HfO₂ could not be determined by XRD because its diffraction pattern is superimposed with that of ZrO₂ which possesses identical crystal cell.

To complete the analysis the FTIR spectra of this support was registered. The zirconia spectrum, depicted in Fig. 2a, indicates the presence of ZrO₂ and the isostructural HfO₂, in some extent. In both oxides, having a monoclinic structure, the contributions to the bands are attributed to Zr-O (and Hf-O) vibrations from the ZrO₇ (HfO₇) units present in the structure. The six characteristic bands of zirconium oxide can be seen located at: 722, 574, 490, 409, 343 and 258 cm⁻¹. A unique HfO₂ band can be observed at 752 cm⁻¹, the remaining bands (635, 600, 512, 410, 343, 324 and 255 cm⁻¹) belonging to this oxide are hidden behind those of zirconium oxide (24).

These features are in accordance to the low proportion of HfO_2 present in the raw material, as already discussed.

Regarding sulphate doped zirconia, the amorphous nature of this material was confirmed by its XRD pattern, as can be seen in [Fig 1b](#) it shows pronounced diffuse peaks at 2θ : 20° and 50° , around the typical signals belonging to tetragonal ZrO_2 (JCPDF N°: 34-1084). The infrared spectrum of hydrated sulphated zirconia depicts the intense and broad high energy band located at 3434 cm^{-1} and at lower energy the signal at 1635 cm^{-1} , attributed to the stretching and deformation of H_2O , respectively. According to [Fig 2b](#), very typical spectral features of sulphate groups also may be observed, since the absorption of SO_4^{2-} appears as an splitted band, with absorptions at 1113 , 1079 and 992 cm^{-1} which are assigned to $\nu(\text{S=O})$ antisymmetric stretching (ν_3). This reflects the low symmetry of the covalent sulphate species present on the surface of the support, in comparison with the free anion, which is characterized by a single band at 1104 cm^{-1} . It has been proposed that the structure of the S=O oscillator is probably of the type $(\text{ZrO})_3\text{S=O}$ [27].

3.2 Textural properties of ZrO_2 and sulphated zirconia

The BET textural properties determined for ZrO_2 and sulphated zirconia are detailed in Table 1. As can be seen, the S_{BET} of SZr shows a large specific area, exceeding $150\text{ m}^2\text{g}^{-1}$. This is a consequence of the sulphation process and amorphousness of this material. In contrast, the surface area of crystalline ZrO_2 is markedly lower and accordingly porosity is also low.

3.3 Characterization of the Zr-supported **CuFe₂O₄** catalysts

3.3.1 Thermal analysis of the precursor

The thermogram of the as-prepared precursor, extracted from the vacuum oven, was registered in order to study its thermal behaviour at high temperature. Analyzing the TG curve shown in [Fig.3](#), which belongs to CiZr30, it can be observed that the decomposition of the precursor takes place in three thermal steps separated by the sharp signals around 145°C and 187°C . According to the synthetic procedure, citric acid is not only a chelating agent but also a fuel and during the heating process of the gel, the nitrates are decomposed and the gel dehydrates and breaks up.

The small weight loss below 145°C is attributed to the vaporization of planar and inner water. This thermal accident is followed by two drastic mass losses of 24% and

34.5%, in the thermal range from 45°C to 300°C, respectively, due to the relief of gases CO₂, H₂O and NO₂ from the thermal decomposition of the precursor. This assignment is supported by the similar results already reported for related materials and catalysts obtained from citrate precursor route [26,27,13]. After these steps the formation of the copper ferrite over ZrO₂ can be assured.

From 300°C to 700°C a very slight mass loss is registered in the thermogram and no other thermal effects are observed in the formed phase, since the TG curve is almost featureless in this thermal interval. All the assignments were confirmed by XRD and FTIR measurements.

In the case of the thermogram of the analogous sample CiSZr30 the general profile is similar, although it shows an additional weight loss, up to 600°C, attributed to the elimination of the sulphate groups from the support.

Finally, it is interesting to compare the thermo-gravimetric data obtained for the supported material with the thermal behaviour of the bulk ferrite precursor obtained by identical synthetic route. In the latter the pyrolytic degradation of the precursor takes place in two steps delimited by a drastic mass loss at 150°C [19]. These evidences suggest that the presence of the support delays the decomposition of the precursor and perhaps some of the mass of CuFe₂O₄ is not supported in certain extent.

3.3.2 XRD analysis of the precursor

The evolution of the phases formed during the firing of the citrate precursor, in the thermal range 150-700°C, for the samples labeled CiZr30-T and CiSZr30-T (T= 150, 400 and 700°C) was more deeply studied by XRD analysis.

In the case of the catalysts supported on zirconia, the structural information obtained from XRD diagrams is limited by the fact that the most characteristic signals of the supported CuFe₂O₄ ferrite are diminished by the strong peaks of the monoclinic ZrO₂, from the support, despite of the metal loading of the catalysts. Furthermore, it is possible to distinguish the characteristic peaks of crystalline Cu-ferrite only in the case of the solid calcined at 700 °C, as may be observed in the [Fig. 4](#). The absence of XRD peaks, belonging to the spinel formed on the zirconia surface, in the catalyst calcined at 150 °C, which was demonstrated by the FTIR study, indicate the amorphousness of the precursor material. Nevertheless at higher temperatures the

crystallinity of Cu-ferrite increases in the same way as in the bulk oxide already studied. On the other hand, the analysis of the relative intensity ratio $\text{ZrO}_2:\text{CuFe}_2\text{O}_4$, demonstrates the correlation with the amount of metallic load in all supported materials, as expected.

According to XRD data of the precursor material of the family CiSZr30-T catalysts, the amorphous nature of this material was confirmed by the lack of diffraction lines in the XRD pattern. When the sample is submitted to calcinations from 150 to 400°C no significant changes were observed, suggesting that the crystallization of Cu-ferrite over SZr is slower than over zirconia, and simultaneously that the support remains amorphous, in this thermal range. Furthermore as can be seen in [Fig 4](#), the diffractogram of CiSZr30-700 the typical signals of tetragonal CuFe_2O_4 are clearly observed. At the same time the main peaks belonging mostly to tetragonal zirconia in coexistence with the monoclinic polymorph of ZrO_2 is confirmed. The tetragonal modification of ZrO_2 is known to be metastable at low temperature and to coexist with the stable monoclinic modification, only if the crystallites are smaller than 30nm. In addition the transformation from tetragonal to monoclinic is complete with the annealing at 1200°C [[22,24](#)]. According to FTIR results, the desulphation of the support accompanies the crystallization of the support, as will be discussed in the next section.

The unit cell parameters calculated for CuFe_2O_4 over the two Zr-supports are similar to the values determined for the bulk tetragonal CuFe_2O_4 , already reported [[19](#)]. Therefore, it could be concluded that the interaction between the spinel and the support is negligible for any metallic loading and that the supports would act mainly as an anchoring for the mixed oxide.

3. 3.3 FTIR characterization of precursor and calcined catalysts

To determine the changes in the chemical environment of the precursor, the FTIR spectra of the precursor and catalyst thermally treated from 150 to 700 °C were recorded, and are shown in [Fig 5](#), for the representative sample CiZr30-T. The spectrum of the solid coming from the vacuum oven was interpreted, taking into account the formation of a tridentate chelate complex with both, Fe^{3+} and Cu^{2+} cations. The IR spectrum of the precursor shows a characteristic absorption of the

hydroxylate bond (O-H) around 3400 cm^{-1} and the peaks localized at 1600 , 1390 and 1060 cm^{-1} which are assigned to the carboxylate group. These results are in good agreement with other metal citrate complexes spectra reported in the literature [28]. After thermal treatment at 100°C , the spectral pattern shows that the absorption bands belonging to the complex precursor remain until its disappearance when the sample is calcined over 150°C . As can be seen in the figure, only the traces of the precursor are detected, whereas the typical broad splitted band, belonging to the support is observed in the low energy region, below 1000 cm^{-1} . When the calcination temperature raises the spectra is completely dominated by ZrO_2 signals. The observed spectroscopic behaviour is in complete accordance with XRD and TG data. As can be seen in Fig. 6, the significant bands belonging to the bimetallic chelate complex, accompanied by those assigned to SO_4^- from the support, are clearly identified in the spectra of the precursor CuZr_3T . When the sample was thermally treated at 400°C , the sulphate bands remained but those belonging to the chelate ferrite precursor have disappeared. Furthermore, when the sample is calcined at 700°C the spectrum is dominated by the broad and intense zirconia absorptions, in the low energy region. The characteristic bands of sulphate are no longer detected in this sample, suggesting that the elimination of sulphate of the Zr-support has occurred. This spectroscopic evidence is supported by XRD results since the peaks of ZrO_2 polymorphs were observed. According to these results, the desulphation process due to calcination, observed by FTIR spectroscopy, promotes the crystallization of the support, giving rise to ZrO_2 , confirmed by XRD diffraction measurements. The typical bands of Cu-ferrite, which are expected at 600 and $\sim 400\text{ cm}^{-1}$, are not observable in anyone of the supported materials due to the complete overlapping with both Zr-support signals. Finally, it seems, by comparison of the spectral patterns of both Cu-ferrite supported materials that the transformation of the precursor into Cu-ferrite requires a higher temperature over sulphated zirconia support.

3.3.4 Textural characterization

In order to analyze the effect of the thermal treatment over the specific surface and pore volume, the textural properties of the supported catalysts were determined and compared with those measured for the supports and bulk CuFe_2O_4 . According to Table 1 which summarizes the specific surface and pore volume for bulk and

supported catalysts, treated at different temperatures, appreciable surface area changes are observed for all the materials.

Some general features are observed. Firstly, as can be seen in the table, the bulk CuFe_2O_4 catalyst synthesized at 400°C depicts a lower surface area in comparison with the supported materials.

Regarding the supported CuZr30-T samples, these display a significant reduction of surface area in comparison with the support. In addition, the thermal treatment up to 700°C for the series leads to a pronounced decrease in the specific surface, even below the values of the support. This effect should be attributed to the sintering of the material which reduces porosity due to the calcinations at high temperature.

On the other hand, the remarkable higher surface typical of SZr, is slightly enhanced in the supported CuZr30-400 material obtained at 400°C , suggesting that the ferrite formation has a negligible effect over the textural properties of SZr. Nevertheless the fact that the loss of the sulphate group takes places over 600°C should be taken into account, since the chemical composition of the support changes.

Consequently, in concern of S_g and V_p of both series of CuFe_2O_4 Zr-supported catalysts, it seems that, at a stated temperature, these properties are mainly influenced by the texture of the supports.

3.3.5 Morphology of the supported catalysts

The morphology of some representative samples was analyzed by SEM-EDAX and the micrographs are shown in [Fig. 7](#). According to this figure it can be observed that the catalyst CuZr30-700 displays irregular grains with undefined edges, showing agglomeration in some extent in a widespread sizes. The magnetic behaviour of ferrites could be responsible of agglomeration [\[Referencia 29\]](#).

In the case of the sample CuSZr30-400 the particles are also irregular and dispersed in their sizes but show somehow more rounded borders. In addition some hollows are also observed.

In order to get a deeper insight regarding the distribution of the metallic cations on the surface of the catalysts, the EDAX scanning of the samples has been registered. In this way, it was observed that Cu and Fe are well dispersed on the grains surface, of both Zr-supports, as well as that the Fe/Cu proportion equal to 2 could be confirmed. Moreover the thermal treatment causes a decrease in the amount of

surface cations which act as active sites for the catalysis, during the annealing procedure.

The presence of nanometric particles in these catalysts obtained by citrate route was confirmed by TEM analysis for the series of CiZr30-T materials. According to the TEM images the samples treated at 400°C most particles are below 60nm, whereas for the materials treated at higher temperatures (700°C) the mean surface diameter is widespread. In the latter an enhancement in the sizes of the particles is observed, since some of them are around 270 nm.

3.3.6 Mössbauer

The Mössbauer spectra of the supported materials labelled CiZr30-T and CiSZr30-T, synthesized at 150°C and thermally treated at higher temperatures, are shown in Figs. 8 and 9, respectively. In addition, Tables 2 and 3 show the corresponding fitting hyperfine parameters for each sample.

The Mössbauer spectrum of copper ferrite is composed of two magnetic sextets (MO and MT) with hyperfine fields (H) assigned to Fe³⁺ cations located in octahedral (B sites) and tetrahedral (A sites) sublattices forming the inverse spinel structure, respectively [18]. (respectively no debería despues de sublattices?)

Despite the two sextets are present in the copper ferrite supported over ZrO₂, the spectra depicted in Fig. 8 a and b, are different. For the material obtained at 150°C the most important signal seems to be a central broad doublet. Additionally a sextet representing 48% of the signal is also observed. Accordingly the spectrum could be fitted with three magnetic sextets and two doublets. Two of the sextets could be assigned to Fe³⁺ cations located in octahedral (Mo) and tetrahedral (Mt) sites and the third one (MR) of lower hyperfine magnetic field (H) suggest a marked degree of relaxation and/or magnetic disorder [30]. The two components of the magnetic doublets (P1 and P2) could be attributed to Fe³⁺ in the surface and in the nucleus of nanometric CuFe₂O₄ particles [31]. The two sextets belonging to CuFe₂O₄ are clearly present in CiZr30-700 and their spectral areas representing around 97% of total resonant signal. The similarity of occupation of octahedral and tetrahedral sites of the Fe³⁺ cations suggests that a partially inverted spinel structure was achieved, as already observed for the bulk material [19]. The remainder 3% of the total area is a paramagnetic doublet assignable to Fe³⁺ present in nanometric particles of CuFe₂O₄

with blocking temperature below the ambient [32]. A partial degree of inversion is interpreted based on % spectral areas of MO and MT detailed in Table 2.

According to Mössbauer results these suggest that copper ferrite is probably present in a wide distribution of particle sizes on the zirconia surface, in accordance with TEM analysis.

Regarding the Mössbauer spectra of catalysts supported over CitSZr-30-T, thermally treated at 150 and 400°C, these show a typical profile consisting of only a central signal that was adjusted with a paramagnetic doublet whose hyperfine magnetic belong to Fe³⁺ species . In addition in Table 3 are detailed the fitting parameters for each sample.

The evidence that the whole signal is paramagnetic at room temperature could indicate that the particles, probably of CuFe₂O₄ are present in tiny sizes, placed inside the zirconia structure. In order to confirm this evidence it would be necessary to register the spectrum at a temperature lower than the blocking temperature.

3.3.7 Hydrogen TPR results

The H₂ TPR profiles of Zr supported CuFe₂O₄ prepared by citrate route, treated at different temperatures, were analyzed. The plots belonging to these materials are depicted in Fig. 10 and 11, for the catalysts supported over ZrO₂ and SZr, respectively.

As can be observed in Fig. 10, all the samples exhibit two distinctive peaks. The first signal appearing in the thermal range 300-400°C was assigned to the reduction of CuFe₂O₄ to metallic Cu and to the subsequent reduction of Fe₂O₃-hematite to Fe₃O₄-magnetite [17]. The peak located at high temperature, over 500°C, is attributed to the reduction of Fe₃O₄ to FeO, followed by the reduction to metallic Fe. These results are in accordance with previously reported assignments [17,33].

The temperature of the first TPR peak is expected to provide information on the relative reactivity of their lattice oxygen, therefore the lower the peak temperature, the higher the reactivity. According to the data obtained, the first peak located at 385°C in the bulk CuFe₂O₄ is markedly shifted towards lower temperatures, at around 280°C, suggesting that the supported catalysts contain more reducible Cu and Fe species. Furthermore in the sample labelled CitZr30-150 a splitted signal is observed suggesting that this reduction occurs in two steps. The peaks of hydrogen

consumption, located over 500°C, are also slightly splitted which would indicate that the reduction of magnetite also takes place in two steps.

For CiSZr-30-T samples, the TPR curves of the materials thermally treated at 150 and 400°C display the important reduction peak at around 280°C, and a medium intensity signal at 500°C with a shoulder, which are accompanied by a low peak, over 600°C, attributed to the reduction of the sulphate groups present in the support. In fact, in the sample labelled CiSZr-30-700 the disappearance of the last peak is noticeable, because, as it was already demonstrated by FTIR the support is completely desulphated after the thermal treatment at 700°C.

Furthermore, an enhancement of the redox efficiency in the supported materials is assumed due to the larger temperature differences between the two reduction peaks in these materials in comparison with bulk CuFe_2O_4 .

4. Propane combustion activity of the catalysts

The propane combustion was analyzed, in presence of NO traces, using the catalysts supported over ZrO_2 and sulphated ZrO_2 , and it was observed, for a given ferrite content, that the support and the calcinations temperature have an influence on the catalytic activity. In this way it was observed that the catalytic activity shows a gradual enhancement when the % of CuFe_2O_4 increases up to the limit of 30%. In advance, this behaviour could be explained as due to the presence of a higher amount of active sites available on the supported catalysis. Nevertheless, when the load reaches 50%, a sharp decrease for HC conversion, similar or somehow lower than bulk CuFe_2O_4 was observed, suggesting that perhaps not all the mixed oxide is supported. This evidence could be demonstrated by SEM and TEM analysis, since some free CuFe_2O_4 particles, unsupported, have been detected in coexistence with the supported catalyst. Furthermore for a load higher than 30%, the system would behave as a composite material showing a decline in the catalytic performance due to the presence of unsupported ferrite particles.

Based on these experimental results, the catalytic behaviour of the supported materials containing 30% of CuFe_2O_4 , was analyzed in order to establish the effect of the support and the thermal treatment. The plots of propane conversion to CO_2 as a function of temperature are shown in Fig. 12, for the samples labelled CiZr-30-400 and CiSZr-30-400. As can be seen the curves for both catalysts annealed at the same temperature, are identical and display improved catalytic behaviour in

comparison with the bulk Cu-ferrite since the conversion profiles of the supported materials are shifted to lower temperature, reaching total conversion at around 500°C. According to these conversion data, despite of the difference in the physical-chemical characteristics of the Zr supports, both Zr-supported CuFe_2O_4 treated at 400°C, behave as active catalysts for propane combustion. This evidence suggests that the support have a negligible effect on the catalytic properties when the catalysts are treated at this temperature. Indeed, in SZr supported materials this could be explained due to the amorphousness of the support, which displays a very large BET surface area available for the catalytic reaction. On the other hand, in the case of the ferrite supported over ZrO_2 the presence of CuFe_2O_4 nanoparticles, observed by TEM, with inverted spinel structure, according to Mössbauer, could favour the availability of catalytic sites over the support.

To quantitatively compare the **catalysts activities**, Table 3 details the temperature values to reach 50% (T_{50}) propane conversion to CO_2 and H_2O , over the different supported catalysts, treated in the thermal range 150-700°C. The effect of the thermal treatment was subsequently analyzed. According to these conversion data and considering the temperature at which the samples have been treated, a decline in the activity, when the temperature of annealing of the catalysts increases, is observed as a general trend.

The lower values for T_{50} measured for the samples CiZr30-150 and -400, in comparison with the sample submitted to 700°C, is compatible with an increase in the crystallinity of CuFe_2O_4 and size of the particles, originally nanometric, a reduction of the BET surface of catalysts, accompanied by a decrease in the reducibility of the materials upon calcination.

On the other hand for the series of catalysts labelled CiSZr30-T, the correlation between catalytic behaviour and temperature of annealing is more difficult to explain due to the fact that the desulphation of the support upon heating, over 600°C, confirmed by FTIR, leads to the crystallization of ZrO_2 , observed by XRD, which causes a significant change in morphology and redox behaviour. Furthermore a sharp increase in T_{50} , of almost 200°C, was detected for the catalyst annealed at 700°C.

In summary, the discussed data confirm that for the family of Zr-supported CuFe_2O_4 catalysts investigated, the catalytic activity is dependent on the temperature of activation and the characteristics of the Zr-support. Indeed, the thermal treatment

affects the size and **crystal degree** of the Cu-ferrite particles; and in the case of SZr supported samples a change in the structure of the support, due to desulphation, around 600°C.

It is also interesting to make a further comparison of the activity of these Zr-supported catalysts with other related materials, reported to be highly active for propane combustion. In the work reported by Choudhary et al. [21] which describes the combustion of dilute propane over a series of transition metal-doped ZrO₂ (cubic) catalysts (metal/Zr mole ratio 0.25, being metals: Co, Mn, Cr, Fe and Ni) at the same space velocity (51,000 cm³g⁻¹h⁻¹) have found T₅₀ values between <450-325°C>. In addition among these catalysts Co-doped ZrO₂ depicts the best performance, attributed to a significant increase in the mobility of oxygen in the crystal lattice. Furthermore, the T₅₀ reported for the Fe-doped ZrO₂ phase was ~400°C, a value intermediate between the measured for CiZr-30-400 and -700°C, as can be seen in Table 4.

Regarding the combustion of propane over supported noble metals catalysts, several studies have been reported by Garetto [34]. According to this, similar values of T₅₀ have been established for the system Pt/MgO (443°C) and Pt/Al₂O₃(357°C); whereas a markedly lower value, around 100°C below, has been reported for Pt supported over acid zeolites, also tested for propane combustion.

In the light of these results is demonstrated that Zr-supported CuFe₂O₄ catalysts, over ZrO₂ and sulphated ZrO₂, display an efficient catalytic activity for HC combustion, particularly propane, which is comparable to that of the noble-metal-supported materials, possessing the advantage of being much cheaper and moreover resistant towards poisoning.

5. Conclusion

6. Bibliografía

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