



**PREPARATION AND CHARACTERIZATION OF AN AB₂O₄ SPINEL TYPE
OXIDE: CATALYTIC APPLICATION OF THE SUPPORTED CuFe₂O₄
SOLID.**

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Abstract

In this paper, the effect of the support on the catalytic behavior of CuFe₂O₄ mixed oxides, supported on ZSM-5 and Al₂O₃, for a ferrite/support relation of 30%, is analyzed. The supported Cu ferrite was obtained by impregnation of the supports with Cu and Fe nitrates solutions and adding citric acid, for calcination temperatures between 150 and 700°C. The propane combustion

was used as reaction test. The catalytic activity was determined in a fixed bed flow reactor at programmed temperature, with a flow of 100 cm³/min containing a mixture of oxygen 4% and propane 1000 ppm. The addition of 500 ppm of NO in the feed resulted in different effects in the reaction. The zeolitic catalysts demonstrated to be active for the reduction of NO to N₂, as well as for the oxidation of propane to CO₂. The ferrite supported on Al₂O₃ only showed activity for the propane oxidation to CO₂. For both materials, the propane conversion, in presence of NO in the feed, is shifted towards lower temperatures suggesting that the hydrocarbon activation is modified by the presence of NO.

Keywords: Cu ferrite, propane combustion, supported mixed oxides.

Resumen

En este trabajo se analiza el efecto del soporte sobre el comportamiento catalítico de óxidos mixtos de CuFe₂O₄ soportados sobre ZSM-5 y Al₂O₃ para una relación ferrita/ soporte igual al 30%. La ferrita de Cu soportada fue obtenida por impregnación de los soportes con solución de nitratos de Cu y Fe, adicionando ácido cítrico, para temperaturas finales de síntesis entre 150 y 700°C. La combustión de propano, fue empleada como reacción test. La actividad catalítica se determinó a temperatura programada en un reactor de flujo a lecho fijo con un caudal de 100 cm³/min conteniendo una mezcla de 4% de oxígeno y 1000 ppm de propano. El agregado de 500 ppm de NO en la alimentación produjo diferentes efectos en la reacción. Los catalizadores zeolíticos mostraron ser activos para la reducción de NO a N₂ y la oxidación de propano a CO₂. Las muestras soportadas sobre Al₂O₃ sólo presentaron actividad para la oxidación del propano a CO₂. Ambos materiales muestran que la conversión de propano en presencia de NO en la alimentación se desplaza hacia menores temperaturas sugiriendo que la activación del hidrocarburo es modificada por la presencia de NO.

Palabras clave: ferritas de Cu, combustión de propano, óxidos mixtos soportados.

Introduction

The catalytic combustion of hydrocarbons is of great interest from the point of view of the environment as well as of the energy production. The catalytic combustion has the advantage of producing insignificant amounts of secondary contaminants (NO_x, CO, etc) and enhancing the energy efficiency. Recently, Choudhary et al [1] have presented a review on combustion of light hydrocarbons in which there is a reference to catalysts of noble metals and metallic oxides (spinel, perovskites, doped oxides, etc.). In the last years, research has been carried out on mixed oxides of transition metals, of the type A^{II}B₂^{III}O₄ with spinel structure, which are active and thermally stable. In addition to this, there is great availability of raw materials necessary for their synthesis. The main advantage of transition metallic oxide catalysts is their low cost in comparison with the noble metals, traditionally used for this purpose. Some of them have proved to catalyze efficiently CO to CO₂ [2-4] oxidation, the combustion of organic compounds [5, 6, 11, 12], the reduction of NO_x by hydrocarbons or particle material [7-10] and the methanol reforming [13]. The oxidic materials containing Cu, Co, Fe and Cr are potentially interesting for the catalytic combustion of hydrocarbons [14] since they have a relatively high activity and an acceptable stability. In a previous work [15], the influence of the ferrite CuFe₂O₄ content and the synthesis temperature on the activity, were determined.

The aim of this work is to analyze the influence of the support on the catalytic behavior of Cu ferrite during propane combustion and to correlate it with the structural characterization by Mössbauer spectroscopy, DRX and FTIR.

Experimental

The $CuFe_2O_4$ catalysts were prepared using citrate method, therefore a solution of citric acid, in the appropriate relation to metals, was added to an aqueous solution containing stoichiometric amounts of $Cu(NO_3)_2 \cdot 3H_2O$ (Riedel-de Haën) and $Fe(NO_3)_3 \cdot 9H_2O$ (Malinckrodt). The impregnation of the supports (ZSM5 and Al_2O_3) was carried out for 4 h with magnetic stirring. After the impregnation, the evaporation was completed, first in a sand bath at $70^\circ C$ and finally under vacuum at $85^\circ C$. The obtained solid was ground and heated in a furnace at $150^\circ C$, $400^\circ C$ and $700^\circ C$ during 4 h. respectively, with intermediate grindings every hour.

The catalysts were labeled as CiX-30-T, where X identifies the support, the numbers indicate the ferrite percentage and T the temperature at which they were treated, respectively. The percentage of active component and temperature was chosen according to a previous report [15].

The samples were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Mössbauer Spectroscopy and Temperature Programmed Reduction (TPR).

The analysis by XRD was carried out using a Philips PW 3710 diffractometer with Cu anode and graphite monochromator. FTIR spectra were recorded on a Nicolet-Magna 550 equipment, with CsI optics, applying the "pellets" KBr technique.

The active species were determined by TPR in a conventional flow reactor, fed with 20 ml/min of a $N_2:H_2 = 9:1$ mixture for a solid sample of 30 mg. The temperature varied between 100 and $800^\circ C$, at a rate of $10^\circ C/min$.

The Mössbauer spectra, recorded at room temperature, were obtained in transmission geometry, with a 512 channel constant acceleration spectrometer. A ^{57}Co 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. The Mössbauer spectra were evaluated using of a commercial fitting program named Recoil, using Lorentzian lines. All spectra were folded to minimizing geometric effects.

The catalytic evaluation was carried out in a fixed bed flow reactor containing 0.12 g of catalyst, a total flow of $100\text{ cm}^3/min$, in a temperature range from $200^\circ C$ up to total conversion. The mixture feeding the reactor was formed by 1000 ppm propane, 4% O_2 and He as balance. The reactor feed and effluent were analyzed by an "on-line" Shimadzu GC-8A chromatograph, with thermal conductivity detector, using a CTR1 column (Alltech) at $40^\circ C$.

Results and Discussion

X-ray diffraction results.

The XRD patterns of the supported catalysts were analyzed taking into account the thermal decomposition results of the bulk catalyst, obtained by the same synthetic procedure. According to these previous studies, the material taken from the vacuum oven is amorphous, consisting of particles at nanometric scale that evolve, by thermal decomposition of the precursor complex, at $150^\circ C$ towards $CuFe_2O_4$ spinel phase, with tetragonal structure, of very low crystallinity. According to the XRD analysis, the bulk catalyst reaches the highest crystallinity and particle size at $700^\circ C$.

The XRD patterns of samples supported on zeolite are shown in Figure 1. As may be observed from the general features of the X-ray diffractograms of these catalysts, the characteristic peaks of the zeolitic support are maintained in the precursor, as well as in the material thermally treated at high temperature. However, a significant decrease of crystallinity in the zeolitic support of the catalyst is observed in the diffractogram of the precursor material extracted from the vacuum oven. Surely, this feature is due to the impregnation process on the support with the Fe/2Cu citrate

complex. Furthermore a change in the intensity relation I/I_0 of the most intense peaks is observed, since these are reversed.

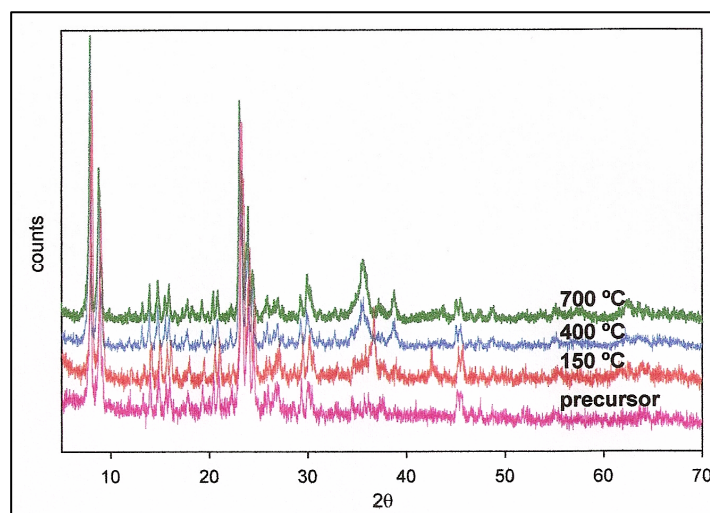


Figure 1. Diffractograms of the catalysts supported on ZSM-5, at each synthesis temperature.

The main changes in DRX are detected in the region located in 2θ between $30-45^\circ$, when the precursor undergoes pyrolysis between $150-700^\circ\text{C}$. The DRX of the material treated at 150°C shows peaks characteristic of the zeolitic support which keep its crystallinity in relation to the precursor, and also the appearance of two new diffractions lines, of moderate intensity, at $2\theta = 36.7^\circ$ and 42.5° , which are attributed to copper oxide. It is also observed the beginning of the recovery of I/I_0 values belonging to the support.

After calcination at 400° , it is observed the disappearance of the peak at $2\theta = 42.5^\circ$ and the other signal at $2\theta \approx 37^\circ$ is splitted in three peaks of moderate to low intensity, with the first peak shifted towards low diffraction angles. Thus, this is attributed to the formation of the ferrite phase. From 700°C , this signal increases its intensity, surely due to the crystallinity increase of the phase formed. Regarding the DRX signals, assigned to the zeolitic structure, these considerably increase their intensity in the thermal range $400-700^\circ\text{C}$, but without reaching the crystallinity of the original support. Nevertheless, the complete recovery of the intensity relation I/I_0 is achieved.

On the other hand, the diffractograms of the materials supported on alumina at 150°C , simply, show the characteristic peaks belonging to the support and to the spinel structure. The support diffraction lines do not undergo significant changes during its impregnation and subsequent thermal treatments. Only a progressive increase of crystallinity can be observed as the synthesis temperature rises, for both the ferrite and the support.

FTIR Spectroscopy Characterization

Figure 2 shows the spectra of the samples supported on zeolite. The spectrum of the precursor material, when taken from the vacuum oven, shows the typical bands of the support associated to the skeleton of the ZSM-5 aluminosilicate. It can be observed the most intense band of the spectrum, splitted in 1227 and 1099 cm^{-1} , due to the stretching of Al-O-Si bonds of the tetrahedral building units forming the structure. The deformation modes of the same polyhedra can be observed, with medium intensity, below 600 cm^{-1} . The wide absorption in the high energy

region of the spectrum, centered at 3435 cm^{-1} , resulting from $-\text{OH}$ stretching, is associated to the vibration of water molecules coordinated to zeolite structure. In addition, the HOH deformation mode of the same bonds is placed in 1600 cm^{-1} . It is worth mentioning that in catalysts supported on zeolite, these bands are overlapped with the vibrations belonging to the same species presents in the precursor when it is taken from the vacuum heater. The broadening of the 3435 cm^{-1} band towards lower frequencies may be due to the formation of H bridges in the precursor, which subsequently disappear with the thermal treatment.

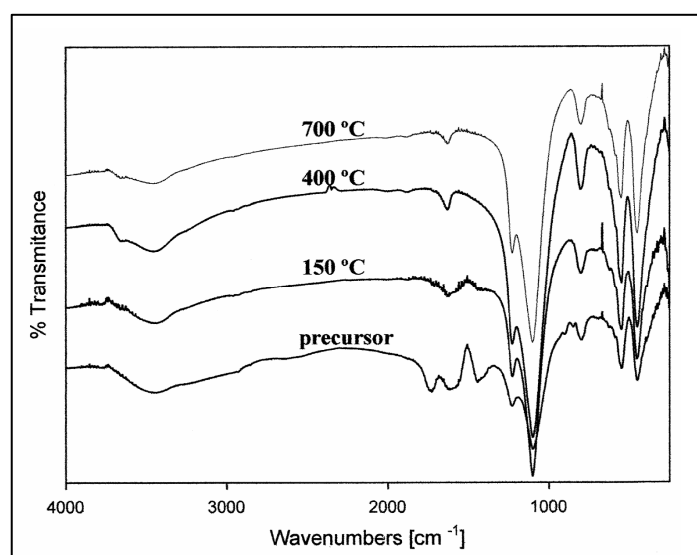


Figure 2. FTIR Spectra of the catalysts supported on ZSM-5.

The absorptions associated to Fe/Cu complex with citrate, formed on the support surface and cavities, can be observed in the middle region of the spectrum. The frequencies around 1620 and 1442 cm^{-1} , assignable to the functional groups present in the Fe/2Cu complex, as well as a band due to the free ligand centered in 1727 cm^{-1} , are noticeable.

By comparison with the spectra of other precursor materials, without silico-aluminate structure, it is observed that the main bands of the citrate complex appear in the same positions. Thus, it may be inferred that the bimetallic complex formed by impregnation, when taken from the vacuum oven, are identical to the other supported catalytic materials.

After the thermal treatment at 150 °C , the main absorption attributed to the complex have disappeared, and only one weak signal is detected close to 1440 cm^{-1} , indicating the complete thermal degradation of the precursor. The IR spectra of the samples do not show significant changes in the thermal range between $400\text{--}700\text{ °C}$, except for the modifications that are observed in the stretching band $-\text{OH}$, in the high energy region of the spectra. After this thermal treatment, a clear signal at 3650 cm^{-1} probably due to the vibration of bridge oxhydriles of groups $\text{Si}(\text{OH})\text{-Al}$, corresponding to Brönsted acid sites, not observable in materials below 400 °C , is now distinguishable. The existence of intense bands below 600 cm^{-1} , corresponding to deformational modes of the condensed polyhedra AlO_4 and SiO_4 , forming the zeolitic lattice, restrain the detection of the bands associated to spinel mixed oxides that absorb in the same spectral region.

Figure 3 shows the spectra of catalysts supported on $\alpha\text{-Al}_2\text{O}_3$ at each synthesis temperature. In the spectrum of the material treated at 150 °C , the weak bands at 3435 cm^{-1} are due to H-OH stretching, whereas the signal around 1600 cm^{-1} can be assigned to the H_2O angular deformation.

The bands of the remaining precursor are slightly observed at 1380 cm^{-1} . In the low energy region, the two bands belonging to the support are very clearly seen. The intense band splitted at 639 and 595 cm^{-1} is due to the bond stretching of AlO_6 octahedra, although the Fe (III)-O stretching bands are also located in this region as it is expected in inverse spinel. The triplet at 487 , 449 and 384 cm^{-1} is associated to the deformational modes of the same polyhedron.

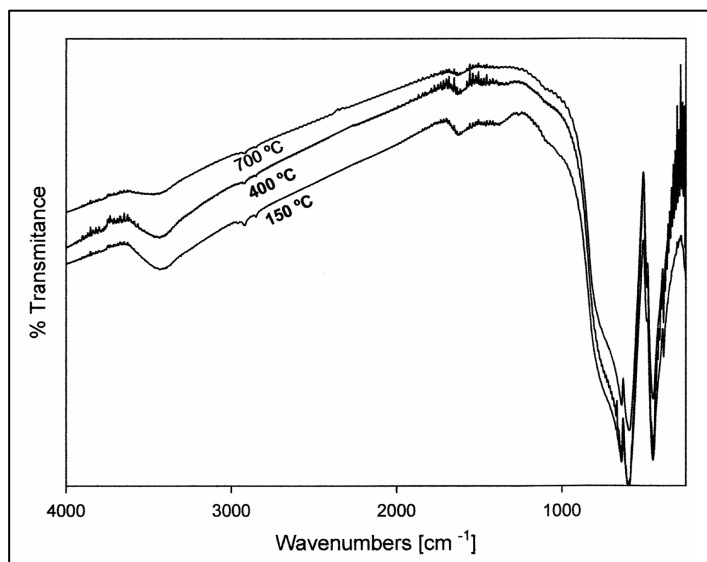


Figure 3. FTIR Spectra of the samples supported on alumina at each temperature.

Mössbauer Spectroscopy analysis

The Mössbauer spectra, recorded at room temperature, of the fresh catalysts supported on zeolite ZSM5 (CiZe) and on Al_2O_3 (CiAl), synthesized at 150 °C , and containing 30% Cu ferrite, are shown in Figures 4 and 5, respectively. Their corresponding adjustment parameters are also shown in Table 1.

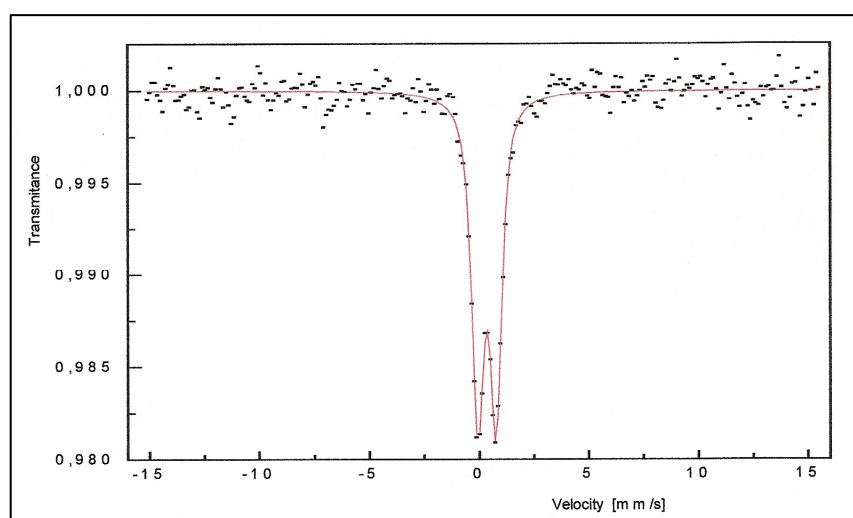


Figure 4. Mössbauer spectra at room temperature of CiZe-30-150 fresh.

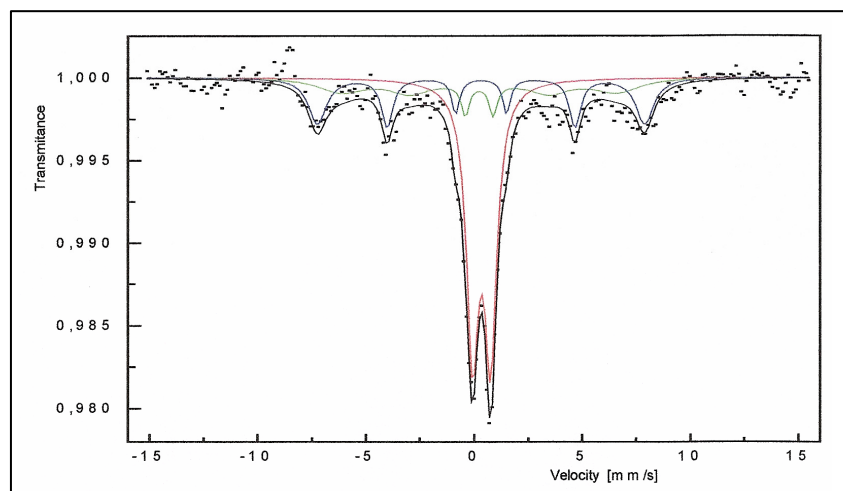


Figura 5. Mössbauer spectra at room temperature of CiAl-30-150 fresh.

Tabla 1. Hyperfine parameters of fresh catalysts, by fitting the corresponding spectra at 298 K.

Catalizador	Parámetros	M_O	M_T	P_1
CiZe	H(T)	—	—	—
	δ (mm/s)	—	—	0.34
	2ε (mm/s)	—	—	—
	Δ (mm/s)	—	—	0.84
	A (%)	—	—	100
CiAl	H(T)	52.0	42.9	—
	δ (mm/s)	0.31	0.22	0.34
	2ε (mm/s)	0	0	—
	Δ (mm/s)	—	—	0.84
	A (%)	26	22	52

References: (H) hyperfine magnetic field, (δ) isomer shift, (Δ) quadrupole splitting, (ε)quadrupole shift, (Γ) line width, (A) relative area

The Mössbauer spectrum of bulk ferrite $CuFe_2O_4$, with tetragonal structure, is composed by two magnetic sextets (M_O and M_T) with hyperfine fields (H) of 51.0 and 48.2 T, at room temperature, which correspond to Fe^{3+} ions located in octahedral (Sites B) and tetrahedral (sites A) holes of the lattice [15,16].

The catalyst CiZe shows only one central signal that was fitted with a paramagnetic doublet which hyperfine parameters correspond to Fe^{3+} species. In order to carry out a more specific assignment of this species it would be necessary to obtain the spectrum at lower temperatures. However, the fact that the entire signal is paramagnetic at room temperature could indicate that the particles, surely of $CuFe_2O_4$, with small sizes, could be located inside the zeolite channels. The spectrum, registered at temperatures lower than the blocking temperature, could verify this conclusion.

A central doublet and a sextet, both of broad lines, can be observed in Mössbauer spectrum, at room temperature, for the catalyst CiAl. The curvature at the bottom of the signal is indicating the presence of super paramagnetic relaxation. This spectrum was adjusted with a doublet and two sextets. According to the hyperfine parameters obtained by the fitting, the doublet is assigned to Fe^{3+} of the spinel present as small crystals and the two sextets are assigned to Fe^{3+} , occupying tetrahedral and octahedral holes of bulk CuFe_2O_4 . The existence of relaxation could indicate that there is a spread distribution of the spinel particle size.

Hydrogen Reduction at Programmed Temperature results

The reducibility of the samples supported on zeolite is presented in Figure 6. The peaks at low temperatures are assigned to the CuFe_2O_4 reduction to Cu^0 and Fe_3O_4 , and the peak at higher temperature is assigned to Fe_3O_4 reduction to Fe^0 , in agreement with references [17-19]. The supported samples present two signals at lower temperature, whereas the bulk material shows a well-defined peak at 385°C . The difference can be attributed to the copper location in the different zeolite structural sites. The signal around 240°C is assigned to the Cu^{+2} to Cu^{+1} possible reduction [20].

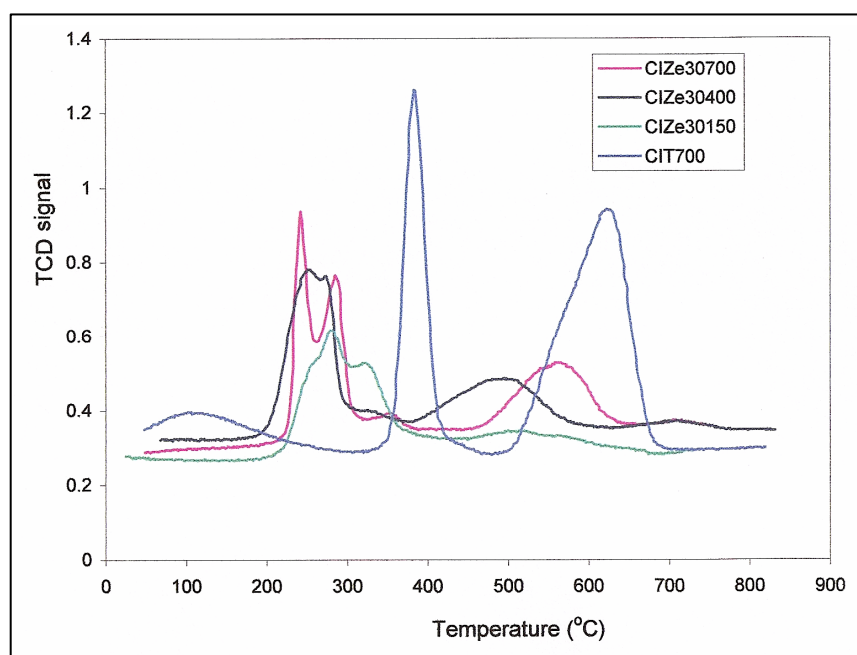


Figure 6. TPR profiles of CuFe_2O_4 , supported on zeolite ZSM-5.

The reduction diagrams on CuFe_2O_4 supported on alumina are represented in Figure 7. This is similar to that observed for CuFe_2O_4 bulk. The presence of the support does not seem to modify the ferrite structure although the reduction temperature increases with the synthesis temperature, without reaching the values of the bulk material.

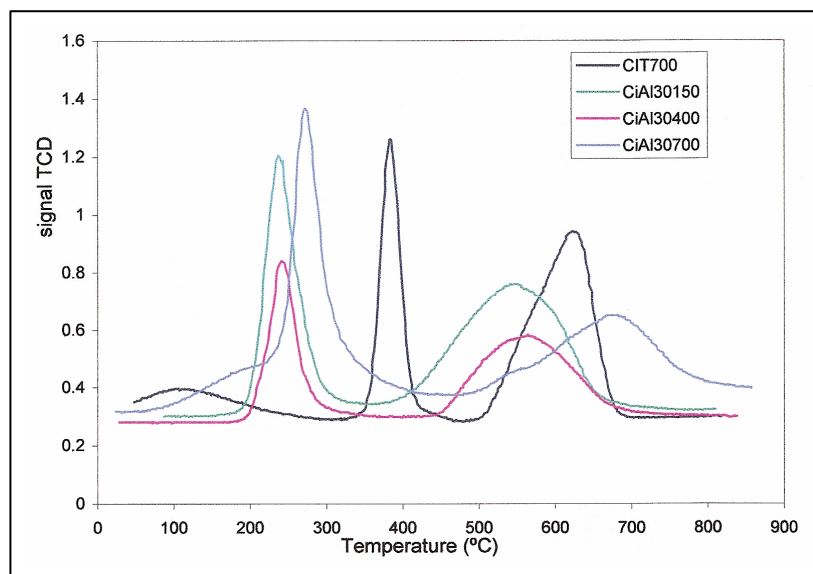


Figure 7. TPR profiles of $CuFe_2O_4$ supported on alumina.

Catalytic Performance tests

The propane combustion was analyzed, in presence of NO traces, for the catalysts supported on ZSM5 and alumina. It was observed that both the support and synthesis temperature influence the catalytic activity. In Figure 8 is shown the conversion to CO_2 as a function of the temperature for the supported catalysts, synthesized between 150 to 700°C. It is noticeable that the catalysts supported on alumina (CiAl) show lower activity than the material supported on zeolite (CiZe), and that both series increase their activity as the synthesis temperature decreases. In order to compare quantitatively the catalysts activities, the temperature values to reach 50 (T_{50}) and 90% (T_{90}) of propane conversion to CO_2 and H_2O for different catalysts, are shown in Table 2.

The catalysts supported on zeolite (CiZe) also show activity for the NO reduction by propane in agreement with the studies referred to exchanged Cu catalysts on ZSM5 [20]. However, in the case of CiAl catalysts, this reaction is totally inhibited.

As above discussed, TPR data seem to suggest that part of Cu of the catalyst CiZe is in the exchangeable positions in zeolite, which could enhance the NO reduction.

In Table 3, it is shown the maximum conversions of NO to N_2 and the reaction temperature for that conversion value. It is observed that the increment of synthesis temperature increases the NO conversion, in agreement with greater hydrocarbon availability by decrease of combustion reaction (Figure 8).

Table 2: Reaction temperatures for obtaining 50 and 90 % of propane conversion.

Catalizador	CiZe-150	CiZe-400	CiZe-700	CiAl-150	CiAl-400	CiAl-700
T_{50}	311	365	420	365	459	471
T_{90}	374	460	505	482	480	576

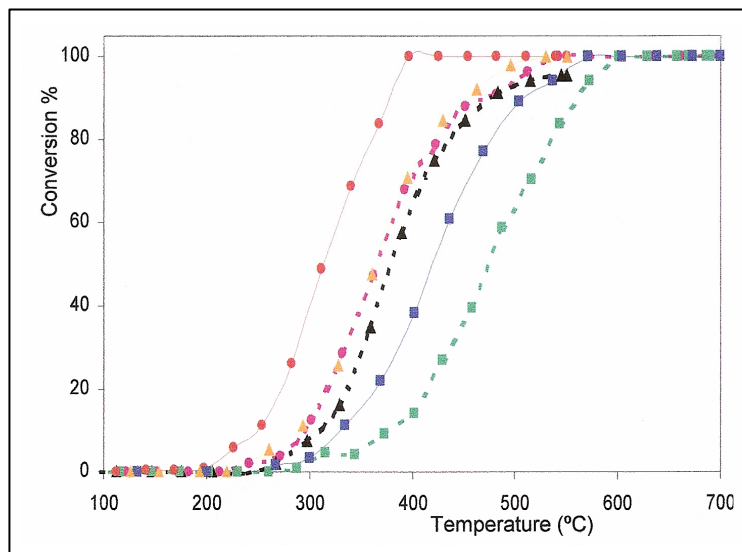


Figure 8. Propane conversion for CuFe_2O_4 (30%) catalysts supported on ZSM5 (full line) and Al_2O_3 (dotted line). Reference: CiZe-150(red), CiZe-400 (orange), CiZe-700 (blue), CiAl-150(violet), CiAl-400 (black), CiAl-700 (green).

Table 3. NO reduction by propane.

Catalysts	NO conversion (%)	Highest Temperature ($^{\circ}\text{C}$)
CiZe-150	14	340
CiZe-400	19	400
CiZe-700	29	503

Conclusions

The results of this paper enable us to conclude that the compounds CuFe_2O_4 supported on the two chosen solids (ZSM5 and $\alpha\text{-Al}_2\text{O}_3$) behave as active catalysts for the propane combustion. This behavior is more significant for samples supported on ZSM5, especially in those materials synthesized at 150°C . The ferrite supported on zeolite material also shows reducing activity for the NO present in the medium. These results can be related with to the mixed oxide properties such as a lower crystallinity, the existence of CuFe_2O_4 nanoparticles and a better surface dispersion, observed in these samples by Mössbauer spectroscopy.

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