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# Promotion effect of Ce or Zn oxides for improving furfuryl alcohol yield in the furfural hydrogenation using inexpensive Cu-based catalysts



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# A R T I C L E I N F O A B S T R A C T Keywords: Kerolite/Mg-smectite mixed layer was used as inexpensive material to support metallic copper, with metal loadings (5–30 wt.%). These catalysts are active in gas-phase furfural hydrogenation, maintaining conversion values higher than 80 mol%, at 210 °C, after 5 h of time-on-stream, with high copper loading (15–30 wt.% Cu) catalysts, being furfuryl alcohol and 2-methylfuran the only detected products. The incorporation of Ce and Zn as promoters causes a decrease in the furfural conversion, although catalysts become much more selective toward furfuryl alcohol, reaching a maximum furfuryl alcohol yield above 80%, at 190 °C, after 5 h of TOS, after CeO<sub>2</sub> addition.

# 1. Introduction

Nowadays, the world population is looking for and developing alternative energy sources to the traditional fossil fuels, due to progressive depletion. Moreover, their combustion leads to the emission of harmful gases provoking adverse effects on population and environment. Last decades, several sustainable energy sources have been proposed to replace them, but, individually, these are not able to supply the world energy needs for themselves, so it is necessary the complementary use of these different energy sources.

Biomass is becoming a very important alternative energy and carbon-based chemicals source [1], due to its availability on Earth, although this must not interfere with the food chain to be a sustainable option. Lignocellulosic biomass is considered the main non-edible biomass feedstock, which is composed by cellulose (40–50%), lignin (15–25%) and hemicellulose (20–35%) [2]. Among them, hemicellulose has high potential since its hydrolysis and dehydration can give rise to furfural, which is considered as a building block molecule [2,3].

The presence of an aldehyde group and an  $\alpha$ , $\beta$ -unsaturation in the furan ring confers high reactivity to the furfural molecule. Thus, it can be converted into a large variety of high value-added products via hydrogenation, opening-ring, decarboxylation, oxidation or dehydration reactions [4]. In this sense, hydrogenation of furfural can lead to furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL), 2-

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https://doi.org/10.1016/j.mcat.2018.06.001

methylfuran (MF), 2-methyltetrahydrofuran (MTHF), furan (F), tetrahydrofuran (THF) or C4-C5 alkanes, depending on experimental conditions [2,4]. The furfural hydrogenation can be carried out in gas or liquid phase. Among them, gas-phase is more sustainable, since it is a continuous process and requires softer temperature and pressure conditions [2].

The industrial catalyst used in gas-phase furfural hydrogenation is copper chromite; however, the presence of chromium species, which can be highly toxic, and catalyst deactivation are issues that must be overcome for the development of a most efficient catalytic process [5-7]. Several active phases, such as Cu [8-16], Ni [9,17-20], Ni<sub>2</sub>P [21]. Co [22], Pd [9,23,24], Pt [25-27] or Mo<sub>2</sub>C [28-30], have been proposed. The catalytic results have revealed that the hydrogenating character of the active phase is a key factor in determining the activity and selectivity pattern. Thus, the more hydrogenating catalysts, such as those based on Ni or Pd, tend to cleavage the C-C bonds, even the opening ring to obtain alkanes. Moreover, this high catalytic activity can also lead to a faster deactivation. Catalysts with lower hydrogenating behavior, such as Cu, Co, Ni<sub>2</sub>P or Mo<sub>2</sub>C, do not favor the C-C scission, originating MF and FOL as main products. These chemicals have a great commercial interest, since FOL is used in the manufacture of foundry resins due to their excellent chemical, thermal and mechanical properties, synthesis of fibers or dispersing agents, and intermediate for the synthesis of lysine or vitamin C [4,31]. On the other hand, MF possesses a high potential to be used as gasoline additive,

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Received 22 March 2018; Received in revised form 31 May 2018; Accepted 1 June 2018 2468-8231/ @ 2018 Elsevier B.V. All rights reserved.

since increases the octane value (103), the synthesis of heterocycles and solvent in the synthesis of antimalarial drugs or methylfurfural [4,32].

Among metal active phases, copper is the most inexpensive active, and it has been reported in the literature that basic or amphoteric supports, such as MgO [13], ZnO [11] or CeO<sub>2</sub> [12], or even slight acidic, such as clay minerals or silica, improve the catalytic behavior [8–10,15]. In fact, the presence of small Cu particles supported on SiO<sub>2</sub> allows to attain a high FUR conversion, obtaining MF as main product, since the hydrogenolysis of FOL is favored [16,33]. However, supports with stronger acidity do not favor the FUR hydrogenation in gas phase, but FUR polymerizes.

In order to develop sustainable catalysts on a larger scale, inexpensive supports have emerged as alternative. Thus, raw especial clays, such as bentonite and sepiolite, have been proposed as catalytic support due to their high specific surface area and low acidity [15,34]. The present research aims at the preparation of copper supported on a kerolitic clay, a randomly mixed layer formed by disordered turbostratic talc (kerolite) and Mg-smectite (stevensite) [35,36]. Previous research has established that kerolite can be associated to other Mg-rich clay minerals, such as stevensite or sepiolite [35,36]. Considering that Cu/MgO systems have shown to be active in the FUR hydrogenation [13] and the particular characteristics of kerolitic clay, this could be a suitable support for highly dispersed Cu nanoparticles.

This work has also evaluated the influence of the addition of ZnO or  $CeO_2$ , as promoters, on the catalytic performance, because the electronic density of Cu nanoparticles can be modified by the presence of these metal oxides [11,12].

# 2. Experimental section

# 2.1. Reagents

The synthesis of the Cu-based catalysts was carried out using copper nitrate trihydrate, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Sigma-Aldrich, 99%), zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (Merck, 99%), cerium nitrate tihydrate, Ce(NO<sub>3</sub>)<sub>4</sub> 3H<sub>2</sub>O (Aldrich, 99%), ethanol, CH<sub>3</sub>CH<sub>2</sub>OH (Prolabo, 95% vol.), ethylene glycol, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, (Sigma-Aldrich, 99%), sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>(Sigma-Aldrich, 99%).

Kerolitic clay was collected from the Esquivias deposits (Madrid Basin, Spain). Previous research has established that these deposits are composed mostly of mixed layered kerolite-stevensite [35]. More recently, it has also been reported the presence of sepiolite and saponite in the Esquivias deposits [36–38].

Chemicals employed in furfural hydrogenation were furfural (Sigma-Aldrich, 99%), cyclopentyl methyl ether (Sigma-Aldrich, 99.9%) as solvent, and o-xylene (Sigma-Aldrich, 99.9%) as internal standard. The gases employed were He (Air Liquide 99.99%), H<sub>2</sub> (Air Liquide 99.999%), N<sub>2</sub> (Air Liquide 99.999%) N<sub>2</sub>O/He (5 vol.% in N<sub>2</sub>O) and H<sub>2</sub>/Ar (10 vol.% in H<sub>2</sub>, Air Liquide 99.99%).

## 2.2. Synthesis of catalysts

Copper-based catalysts were synthesized by a co-precipitation-deposition method, according to previous research reported in the literature [15]. Briefly, 1 g of kerolitic clay was dispersed under stirring in 75 mL of water for 30 min. Later, a solution composed by 10 mL H<sub>2</sub>O, 20 mL ethylene glycol, 50 mL ethanol and the corresponding percentage of copper precursor, for achieving a final copper loading ranging between 5 and 30 wt.%, was added to the clay suspension. In order to precipitate the Cu-species, pH was increased until pH = 11 by dropwise addition of a Na<sub>2</sub>CO<sub>3</sub> (0.5 M) aqueous solution, at 80 °C. After the addition of the precipitant solution, the resulting solution was cooled and aged at room temperature for 24 h, without stirring. The solid was filtered and dried at 90 °C for 12 h, and calcined at 400 °C for 1 h.

In the case of the catalysts with ZnO or  $CeO_2$ , the synthetic procedure was similar to that previously indicated. The Ce or Zn-species was incorporated, using the nitrate precursor, together with the Cu-species considering a Cu/Ce or Cu/Zn molar ratio equal to 1. The catalysts were labeled as K-*x*Cu, K-*x*CuZn or K-*x*CuCe, where *x* is the wt.% of copper loading.

#### 2.3. Characterization of catalysts

The textural properties were evaluated from the N<sub>2</sub> adsorptiondesorption isotherms at -196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. Prior the measurements, the samples were outgassed overnight at 200 °C and 10<sup>-4</sup> mbar. The surface areas were determined with the Brunauer, Emmett and Teller (BET) equation [39], considering a N<sub>2</sub> cross-section of 16.2 Å<sup>2</sup>. The total pore volume was calculated from the adsorption isotherm at P/P<sub>0</sub> = 0.996, and the average pore size was determined by applying the Barrett–Joyner–Halenda (BJH) method to the desorption branch [40]. The Density Functional Theory (DFT) method was employed to determine the pore-size distributions [41].

H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) experiments were performed with the catalyst precursor (0.080 g), previously treated with a He flow (35 mL min<sup>-1</sup>) at 100 °C, for 45 min. After the sample cooled to room temperature, the H<sub>2</sub> consumption was monitored between 50 and 500 °C in an Ar/H<sub>2</sub> flow (48 mL min<sup>-1</sup>, 10 vol% of H<sub>2</sub>), at a heating rate of 10 °C min<sup>-1</sup>. The water formed in the reduction reaction was trapped by passing the exit flow through a cold finger immersed in a liquid N<sub>2</sub>/isopropyl alcohol bath (-80 °C). The H<sub>2</sub> quantification was registered on-line with a thermal conductivity detector (TCD).

XRD patterns of catalysts were obtained with a PANanalytical X'Pert Pro automated diffractometer. The patterns were recorded in a Bragg–Brentano reflection configuration, by using a Ge (111) primary monochromator (CuKα<sub>1</sub>) and an X'Celerator detector with a step size of 0.017° (2θ), between 2θ = 10 and 70°, with an equivalent counting time of 712 s per step. The crystallite size (D) was calculated by using the Williamson–Hall equation, B cos (θ) = (Kλ/D) + (2 ε sin(θ)), in which θ is the Bragg angle, B is the full width at half-maximum (FWHM) of the XRD peak, K is the Scherrer constant, λ is the X-ray wavelength, and ε is the lattice strain [42]. The analysis (major elements) of untreated kerolite/Mg-smectite was carried out by means of the MagiX X-ray fluorescence spectrometer of PANlytical. A Varian 220-FS QU-106, atomic absorption spectrometer was used for the determination of sodium. Loss ignition was determined at 950 °C.

The particle morphology was studied by Transmission Electron Microscopy (TEM), using FEI Talos F200X equipment (Thermo Fisher Scientific). This equipment combines outstanding high-resolution S/ TEM and TEM imaging with industry-leading energy dispersive X-ray spectroscopy (EDS) signal detection, and 3D chemical characterization with compositional mapping. The samples were suspended in isopropyl alcohol and dropped onto a perforated carbon film grid.

Metal surface area and dispersion were evaluated by N<sub>2</sub>O titration [11,12]. This method is based on the formation of a monolayer of Cu<sub>2</sub>O by oxidation of superficial Cu<sup>0</sup> with a N<sub>2</sub>O flow, according to the reaction:  $2Cu^0 + N_2O \rightarrow Cu_2O + N_2$ . Before analysis, the CuO phase is reduced under a 10 vol.% H<sub>2</sub>/Ar flow (48 mL min<sup>-1</sup>) and a rate of 5 °C min<sup>-1</sup>, until 300 °C during 1 h, for all catalysts except in the case of K15CuCe, which was reduced at 230 °C. Then, samples were purged under a He flow and cooled down to 60 °C. The oxidation of Cu<sup>0</sup> to Cu<sup>+</sup> is carried out by chemisorption of N<sub>2</sub>O (5 vol.% N<sub>2</sub>O/He) at 60 °C during 1 h. Later, the catalyst was again purged with an Ar flow and cooled to room temperature. After this, the reduction of Cu<sub>2</sub>O to metallic Cu was accomplished by raising the temperature up to the aforementioned values for all catalysts (300 °C), except for K-15CuCe catalyst (230 °C).

XPS spectra were obtained with a Physical Electronics PHI 5700 spectrometer with non-monochromatic MgK $\alpha$  radiation (300 W, 15 kV, 1253.6 eV) with a multichannel detector. The spectra were recorded in the constant-pass energy mode at 29.35 eV with a 0.72 mm diameter

analysis area. Charge referencing was measured against adventitious carbon (C 1s at BE = 284.8 eV). The PHI ACCESS ESCA-V6.0F software package was used for the acquisition and data analysis. A Shirley-type background was subtracted from the signals. All of the recorded spectra were fitted with Gaussian-Lorentzian curves to determine more accurately the binding energies of the different element core levels. All samples were stored in sealed vials with an inert solvent to avoid oxidation. The samples were prepared in a dry box under a  $N_2$  flow and analyzed directly without previous treatment, and the solvent was evaporated before the introduction of the samples into the analysis chamber.

## 2.4. Catalytic tests

The vapor-phase hydrogenation of FUR was performed in a fixed bed  $1/4^{\text{``}}$  tubular quartz reactor; the pelletized catalyst (0.325–0.400 mm) was placed at the center of the reactor tube between two layers of glass beads and quartz wool. Before the catalytic test, the catalyst was reduced in situ under a H<sub>2</sub> flow (60 mL min<sup>-1</sup>, Airgas, 99.99%) at 300 °C for 1 h. After reduction, it was cooled to the selected reaction temperature under a H<sub>2</sub> flow (10–60 mL min<sup>-1</sup>). Once this temperature was reached, a flow (3.87 mL h<sup>-1</sup>) of a FUR solution in CPME (5 vol.%) was injected continuously with a Gilson 307SC piston pump (model 10SC). Thus, the WHSV was  $1.5 \text{ h}^{-1}$ . CPME is an environmentally friendly solvent and has been used in different organic reactions; thus, it is a green co-solvent for the selective dehydration of lignocellulosic pentoses to FUR [11,21].

The reaction products were analyzed by gas chromatography (Shimadzu GC-14A) equipped with a Flame Ionization Detector and a CP-Wax 52CB capillary column. The furfural conversion and selectivity were calculated and defined as follows:

Conversion $(\%) =$	mol of furfural converted mol of furfural fed	$\times$ 100
Selectivity $(\%) =$	mol of the product mol of furfural converted	× 100

#### 3. Characterization of catalysts

The reducibility study of the Cu-based catalyst precursors, carried out by H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) (Fig. 1), reveals that the reduction temperature of Cu species increases with the copper content. Thus, the maximum reduction temperature varies between 210 °C for K-5Cu and 257 °C for K-30Cu catalysts. Previous research has pointed out that the sequential reduction  $Cu^{2+} \rightarrow Cu^+ \rightarrow$  $Cu^0$  is difficult to resolve in the H<sub>2</sub>-TPR curves [43,44], so the trend in copper reducibility may be ascribed to the particle size and the interaction copper-support, which are two related parameters. Thus, smaller particles are easily reducible, as could be inferred from the fact that a lower Cu content decreases the reduction temperature. However, the increase of copper content leads to quasi-bulk particles, which are more difficult to reduce.

It has been reported in the literature that the use of an acidic support leads to a stronger metal precursor-support interaction, thus increasing the reduction temperature of metal species [45]. However, in the present study, the incorporation of an amphoteric oxide, such as ZnO, hardly modifies the reducibility of Cu species, only decreasing the reduction temperature from 228 °C to 220 °C (Fig. 1B). However, in the case of the catalyst with CeO<sub>2</sub>, the presence of oxygen vacancies in this rare earth oxide improves the reducibility of copper species, since mobility of these oxygen species promotes spillover process in interfacial sites of CuO-CeO<sub>2</sub> [12,44,45], decreasing the reduction temperature of 300 °C was chosen to reduce the Cu species to Cu<sup>0</sup> maintaining this temperature for 1 h to ensure the total reduction to metallic copper.

Textural properties have been deduced from N2 adsorption-desorption isotherms (Fig. 2). According to the IUPAC, these isotherms can be classified as Type IIb, which are typical of macroporous adsorbents, although the initial strong N2 adsorption points out the existence of micropores [46]. With regard to the hysteresis loop, the isotherms are adjusted to H4-type where the more pronounced uptake at low relative pressures confirms the filling of micropores, together with macropores associated to aggregated crystals. Moreover, kerolitic clay (K) exhibits a high BET surface area (275  $m^2 g^{-1}$ ), which makes it suitable as catalyst support (Table 1). The addition of Cu species causes a progressive drop of SBET values as copper content increases by a decrease of the microporosity, as reveals the *t*-plot and  $V_{mic}$  data (Table 1). The incorporation of Zn or Ce species provokes a more evident decrease of the S<sub>BET</sub> values by the blockage of the micropores. The pore size distribution, determined by the DFT method [41], also shows a decreases of the pore size distribution in the range of 1.0–1.6 nm, which confirms the decay of the microporosity when Cu, Zn or Ce species are deposited on the kerolite (Fig. 3).

On the other hand, powder X-ray diffraction (XRD) patterns (Fig. 4) show a broad band with two components with maximum at  $2\theta = 5.8$ (d-spacing of 1.5 nm) and 8.5° (d-spacing of 1.0 nm) [47]. De Vidales et al. assigned the 1.0-nm reflection to kerolite phase [35], whereas the 1.5-nm reflection was associated to stevensite coexisting with random mixing of these two kinds of layers [48]. According to Martín de Vidales et al. [35], broadening of reflections, the effects of diffraction at low angles, and the irrationality of the diffraction peaks ( $2\theta = 19.5$ , 27.8, 34.9, 53.2 and 60.7°) suggest that these materials are formed by barely coherent domains with a very small number of layers per particle. The absence of interlayer cations in kerolite precludes the incorporation of copper, cerium or zinc species between the 2:1 layers, so these species must be located on the external surface of kerolite or interlayer of stevensite [47]. Nonetheless, the clay mineral used as support displayed a relatively high surface area to be a raw clay mineral, and consequently it is expected that metal species must have a high dispersion. The diffraction peaks at  $2\theta = 19.5$ , 27.8, 34.9, 53.2 and  $60.7^{\circ}$  confirm



Fig. 1. H2-TPR profiles of: (A) Cu-based kerolitic clay with different copper content and (B) Cu-based kerolitic clay modified with CeO2 and ZnO.



Fig. 2.  $N_2$  adsorption-desorption at -196 °C of: (A) Cu-based kerolitic clay with different copper content and (B) Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO.

# Table 1 Textural parameters of Cu catalysts supported on a kerolitic clay.

Sample	$S_{BET} (m^2 g^{-1})$	t-plot <sub>mic</sub> (m <sup>2</sup> g <sup>-1</sup> )	$V_{\rm P}~({\rm cm}^3{\rm g}^{-1})$	$V_{mic} (cm^3 g^{-1})$
К	275	172	0.315	0.081
K-5Cu	217	127	0.213	0.057
K-10Cu	206	118	0.220	0.052
K-15Cu	197	106	0.192	0.048
K-20Cu	176	103	0.193	0.046
K-25Cu	171	91	0.190	0.041
K-30Cu	158	88	0.188	0.039
K-15CuZn	123	56	0.176	0.024
K-15CuCe	118	54	0.208	0.023

the crystalline structure of a phyllosilicate (PDF 00-002-0048). In fact, the  $d_{060}$  reflection at  $2\theta = 60.7^{\circ}$  (1.52 Å) corroborates the presence of trioctahedral clay minerals, with Mg<sup>2+</sup> cations in the octahedral sheet [47].

The incorporation of copper species by precipitation (Fig. 4B), calcination and subsequent reduction gives rise to the appearance of two new diffraction peaks at  $2\theta = 43.4$  and  $50.4^{\circ}$ , assigned to  $Cu^{0}$  species (PDF 98-005-3758). The intensity of these peaks increases, as expected, with the amount to copper incorporated. The co-precipitation of cerium or zinc species together with the copper species in the same step (Fig. 4C) causes a decrease in the intensity of the diffraction peaks attributed to the  $Cu^{0}$  species, which suggests the formation of smaller metal particles. The K-15CuZn catalyst displays new diffraction peaks at  $2\theta = 31.9$ , 34.6, 36.2, 47.7, 56.6, 62.9 and 67.9°, which are attributed to ZnO species (PDF N: 98-015-4487), while the K-15CuCe catalyst shows signals at  $2\theta = 28.7$ , 33.2, 47.6 and 56.4°, due to CeO<sub>2</sub> (PDF 98-015-5606).

The Cu<sup>0</sup> particle size, as determined by the Williamson-Hall method

[42], increases from 12 to 24 nm as the copper percentage raises from 5 to 20 wt% (Table 2). The incorporation of Zn or Ce-species, together with the Cu species, leads to the formation of smaller Cu particles (8–10 nm). As was indicated from their H<sub>2</sub>-TPR profiles (Fig. 1B), the incorporation of ZnO or CeO<sub>2</sub> modify the electronic density favoring the formation of Cu<sup>0</sup> species at lower temperatures, which limits the sintering of the Cu-species.

The morphology of Cu-based catalysts was analyzed by TEM (Fig. 5). Micrographs reveal the presence of lamellar particles of kerolite/stevensite mixed layer, similar to those observed by Pozo and Casas [36]. In all cases, spherical  $Cu^0$  particles deposited on the surface of kerolite are observed with variable sizes, in such a way that average values agree well with those deduced from XRD. Large copper particles are found for high metal loadings, whereas the K-15CuCe and K-15CuZn catalysts (Fig. 5D–E) micrographs show a heterogeneous distribution, i.e. regions where the Cu/ZnO or Cu/CeO<sub>2</sub> are deposited on the surface of kerolite and others with aggregated particles. In addition, the formation of Cu-Ce or Cu-Zn species favors the dispersion of Cu species, thus leading to the formation of small copper particles, as was deduced from XRD (Fig. 4B).

The determination of metallic copper surface by  $N_2O$  titration (Table 2) shows that the dispersion of  $Cu^0$  decreases with the copper content, from 52% for K-5Cu to 2% for K-30Cu, and consequently the metallic surface is lowered. The addition of promoters improves the dispersion of Cu particles and consequently the metallic surface, according to XRD and TEM data.

As regards the surface features, XPS technique can allow to get insights into the chemical nature of catalyst surface. The binding energy values of different surface species in the raw kerolitic clay are typical of trioctahedral phyllosilicates (Table 3) [15]. In all cases, the Cu 2p core level spectra exhibit a band at 932.5–932.0 eV, which is ascribed to



Fig. 3. Pore size distribution of: (A) Cu-based kerolitic clay with different copper content and (B) Cu-based kerolitic clay modified with CeO<sub>2</sub>.



Fig. 4. X-ray diffractograms of: (A) raw kerolite, (B) Cu-based kerolitic clay with different copper content and (C) Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO.

Table 2	
Metal characteristic of the Cu-based catalysts.	

Samples	Cu crystal <sup>a</sup> (nm)	Dispersion <sup>b</sup> (%)	Metal surface <sup>b</sup>		
			$m_{Cu}^2 g_{cat}^{-1}$	$m_{Cu}^{2} g_{Cu}^{-1}$	
K-5Cu	12 (8)	52	1.45	29.1	
K-10Cu	15 (14)	17	0.84	8.4	
K-15Cu	19 (19)	9	0.74	4.9	
K-20Cu	24 (24)	6	0.62	3.1	
K-25Cu	20 (23)	4	0.49	1.9	
K-30Cu	23 (35)	2	0.32	1.1	
K-15CuCe	10 (n.d.)	36	2.71	18.1	
K-15CuZn	8 (8)	22	1.40	9.35	

<sup>a</sup> Cu crystal size obtained from XRD data by the Williamson-Hall method. Data in parenthesis after 5 h of TOS. (n.d.: non-determinated).

<sup>b</sup> Dispersion and metal surface obtained by N<sub>2</sub>O titration.

reduced copper species (Fig. 6A). The absence of the shake-up satellite at 934–935 eV discards the existence of  $Cu^{2+}$  species. However, it is not feasible to discern between the reduced copper species ( $Cu^0$  and  $Cu^+$ ), so it is necessary to study the Auger  $Cu_{LMM}$  signal (Fig. 6B). In spite of the precursors were reduced at 300 °C for 1 h, it can be observed the coexistence of  $Cu^0$  (918.3–918.8 eV) and  $Cu^+$  (917.6–918.0 eV) species, although the  $Cu^0$  is the main contribution in all cases (Table 3). The presence of  $Cu^+$  species could be ascribed to the partial oxidation of the  $Cu^0$  during the sample handling. The surface atomic concentration values raise, as expected, with the copper loading (Table 3), and, in general, they are lower than the corresponding theoretical values, calculated by considering the composition of kerolitic clay determined by XRF analysis (53.94 wt% SiO<sub>2</sub>, 2.66 wt% Al<sub>2</sub>O<sub>3</sub>, 25.26 wt% MgO). This difference can be justified by the large copper particles (8–23 nm) and the thickness analyzed by the XPS technique (2–3 nm), which limits the amount of copper detected by XPS.

The incorporation of Zn or Ce provokes a decrease of the intensity of Cu 2p signals, thus suggesting that the superficial copper could be partially coated by ZnO and CeO<sub>2</sub> (Table 3), as corroborated by the Cu/Ce and Cu/Zn atomic ratios, which are lower to the theoretical ones. The Auger Cu<sub>LMM</sub> study confirms the coexistence of Cu<sup>0</sup> and Cu<sup>+</sup> (Fig. 6D), although the amount of Cu<sup>+</sup> is higher for the fresh K-15CuCe catalyst. The Ce 3d core level spectrum shows a partial reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> about a 15% by the partial (Supplementary Information Fig. 1), which can be attributed to the oxygen mobility of the CeO2 surface and/or the photoreduction of the Ce<sup>4+</sup> species.

# 4. Catalytic results

Copper supported on kerolitic clay catalysts were evaluated in the gas phase furfural hydrogenation, using cyclopentyl methyl ether (CPME) as solvent for furfural, which exhibits higher thermal stability and resistance to acid or basic conditions in comparison to other ethereal solvents, such as tetrahydrofuran or dioxane [49]. In a preliminary test, pure CPME was fed using K-15Cu as catalyst, and the chromatographic analysis of the reaction products ruled out its degradation. Similarly, the raw kerolitic clay without copper was not active.

The evaluation of the influence of copper content on the catalytic behavior at 210 °C (Fig. 7) reveals that, in all cases, catalysts hardly suffer deactivation after 5 h of time of stream (TOS), and FUR



Fig. 5. TEM micrographs of: (A) K-5Cu, (B) K-15Cu, (C) K-30Cu, (D) K-15CuZn and (E) K-15CuCe (Magnification: 100 nm).

conversion increases with the copper content, attaining 90% to K-15Cu catalyst after 5 h of TOS, but the values are always higher than 65%. However, Cu loadings larger than 15 wt.% do not improve the conversion values, but rather causes a slight decrease, reaching similar values (83-87% after 5 h TOS). As regards the reaction products (Fig. 7B-C), FOL and MF were the only hydrogenation products detected. Interestingly, the catalysts with larger copper loading displayed higher FOL yield values, obtaining the highest value of 58% for K-30Cu catalyst, while the catalysts with lower copper content are more selective towards MF. In addition, it is noteworthy how the catalysts with higher Cu content (K-20Cu, K-25Cu and K-30Cu) tend to suffer a loss of MF vield along the TOS, which is accompanied with a progressive increase of the FOL yield. In this sense, it has been reported in the literature that the formation of MF requires higher amount of available hydrogenating sites and/or a slight acidity to favor the hydrogenolysis of FOL to MF [50]. It could be thought that the amount of acid sites of a magnesium clay mineral (trioctahedral), such as kerolite or stevensite, is negligible in comparison to an aluminum clay mineral (dioctahedral), by considering the acid-base nature of the corresponding oxides, so the

formation of MF must be related with the amount of available hydrogenating sites. The hydrogenolysis of FOL to MF generates carbonaceous deposits, which cause the poisoning of active sites responsible of the formation of MF [16].

Fig. 7D shows the FOL/MF selectivity ratio, at 210 °C after 5 h of TOS, for this series of copper-based catalysts. The obtained data reveal that the selectivity pattern is influenced by the copper content. Thus, in general, the catalysts with higher copper content lead to FOL as main product. However, for intermediate copper loading, MF is favored, attaining the minimum FOL/MF selectivity ratio for the K-15Cu catalyst. In this sense, previous authors have pointed out that the size of Cuparticles influences in the catalytic activity favoring both FUR conversion and FOL yield with smaller Cu particles [13].

The incorporation of ZnO or  $CeO_2$  species causes an increase of the metallic surface and by the formation of smaller Cu crystals on the surface of the catalyst. This fact should cause an improvement in the FUR conversion. However the Zn(Ce)/Cu molar ratio of 1, leads to the catalyst deactivation, with a FUR conversion of 65% after 5 h TOS, while the K-15Cu catalyst maintained FUR conversion close to 90%.

Table 3		
Spectral parameters of the C	Cu-based	catalysts

Samples	Atomic Concentration		Percentage Cu s	Percentage Cu species		Surface molar ratio		
	C (%)	Cu (%)	Cu <sup>0</sup>	Cu <sup>+</sup>	C/Cu	Cu/(Si + Al + Mg)	Cu/(Ce or Zn)	
K-5Cu	9.59 (65.38)	1.08 (0.84)	74.4 (42.0)	25.6 (58.0)	0.11 (77.8)	0.033 [0.053] (0.147)	-	
K-10Cu	9.53 (69.29)	1.80 (0.89)	50.1 (43.3)	49.9 (56.7)	0.19 (52.3)	0.055 [0.111] (0.153)	-	
K-15Cu	10.48 (41.37)	2.90 (2.07)	69.7 (33.6)	30.6 (66.4)	0.28 (20.0)	0.093 [0.176] (0.119)	-	
K-20Cu	11.14 (46.32)	3.04 (1.87)	60.6 (38.6)	39.4 (61.4)	0.27 (24.8)	0.102 [0.250] (0.126)	-	
K-25Cu	13.01 (56.52)	3.81 (2.40)	67.2 (33.1)	32.8 (66.9)	0.29 (23.6)	0.131 [0.333] (0.217)	-	
K-30Cu	12.41 (41.66)	5.29 (3.54)	30.2 (61.1)	69.8 (38.9)	0.426 (11.8)	0.188 [0.428] ((0.207)	-	
K-15CuCe	8.36 (29.52)	1.65 (1.56)	39.9 (61.6)	63.1 (38.4)	0.19 (18.2)	0.063 (0.139)	0.44 (0.66)	
K-15CuZn	8.22 (34.86)	1.31 (1.25)	59.9 (48.7)	40.1 (51.3)	0.16 (27.8)	0.039 (0.187)	0.44 (0.49)	

Data in parenthesis after 5 h of TOS at 210 °C, and bulk values (XRF analysis) in brackets.



Fig. 6. (A) Cu 2p core-level spectra and (B) Cu<sub>LMM</sub> Auger signal of the Cu-based kerolitic clay with different copper content. (C) Cu 2p core-level spectra and (D) Cu<sub>LMM</sub> Auger signal of Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO.

This fact is attributed to the incorporation of ZnO or CeO<sub>2</sub> causes modifications in the electronic density for Cu<sup>0</sup> or Ni<sup>0</sup> species since these metals promote the partial reduction of the Zn or Ce species in the form of Zn<sub>1-x</sub>O or Ce<sub>1-x</sub>O<sub>2</sub>, which implies the more obvious electronic perturbation between the transition metal and the metal oxide [11,12,51,52]. Thus, the electronic perturbation together with the decrease of the amount of acid sites from 115 µmol g<sup>-1</sup> for K-15Cu to 46 µmol g<sup>-1</sup> and 27 µmol g<sup>-1</sup> for K-15CuZn and K-15CuCe catalysts, (Supplementary Information Fig. 2) minimizes the hydrogenolysis reaction and the formation of carbonaceous deposits. This fact leads more selective toward FOL, as evidence the FOL yield values, and the formation of MF is lower than 5% after 5 h TOS (Fig. 8).

Taking into account that K-15Cu is the catalyst that exhibits the best catalytic performance in terms of stability and FUR conversion, this was chosen to carry out a more detailed study. The influence of the reaction temperature demonstrates that FUR conversion follows a Gaussian distribution (Fig. 9), in agreement with previous results obtained with copper chromite [53], or other copper-based catalysts [11,13]. Thus, it can be observed that FUR conversion increases with the temperature, reaching the maximum value at 210 °C, but a higher reaction temperature does not favor FUR conversion, since both FUR and FOL molecules tend to polymerize at higher temperatures, leading to the



**Fig. 7.** Evolution of (A) FUR conversion, (B) FOL yield and (C) MF yield as a function of TOS for the Cu-based kerolitic clay with different copper content. FOL/MF selectivity ratio, after 5 h of TOS (D). Experimental conditions:  $T_{Red} = 300$  °C,  $m_{cat} = 150$  mg, T = 210 °C,  $H_2$  flow = 10 mL min<sup>-1</sup>, feed flow = 2.3 mmol FUR h<sup>-1</sup>.

formation of carbonaceous deposits on the catalyst surface, thus deactivating the hydrogenation sites [53]. With regard to the selectivity, it seems clear that FOL selectivity decreases directly with the reaction temperature since hydrogenolysis (FOL  $\rightarrow$  MF) is favored at higher temperature. In spite of the formation of carbonaceous deposits, the K-15Cu catalyst is stable, since it hardly suffers deactivation along the TOS, even at higher reaction temperature.

The influence of the reaction temperature of copper-based catalysts promoted with CeO<sub>2</sub> and ZnO also exhibits a Gaussian distribution, where the maximum conversion values are obtained for a temperature in the range 190–210 °C. Fig. 10 displays the results corresponding to catalysts promoted with CeO<sub>2</sub>. It is noteworthy that the FUR conversion for the K-15CuCe catalyst at 230 °C suffers a drastic drop in comparison to the catalytic tests carried out at lower temperature. As was indicated previously, this lower FUR conversion can be ascribed to the polymerization of FUR at higher temperature, with provokes a drastic deactivation at the beginning of the catalytic process. Moreover, the maximum activity is found at a lower temperature in comparison with the K-15Cu catalyst (190 °C), and selectivity drastically changes, with FOL as the main reaction products and negligible amounts of MF in all the range of studied temperature probably due to CeO<sub>2</sub> and ZnO provides basic sites that minimizes the hydrogenolysis reaction of MF to FOL.

In order to analyze the evolution of the active phase along the TOS, the used catalysts were recovered after the reaction at 210 °C, after 5 h of TOS, and characterized by XRD and XPS. XRD patterns of the used catalysts are similar to those of fresh ones (Fig. 11), ruling out the sintering of Cu<sup>0</sup> particles, or its oxidation. In this sense, the formation of H<sub>2</sub>O as by-product in the FOL  $\rightarrow$  MF reaction could favor the oxidation of Cu<sup>0</sup> to Cu<sup>+</sup> species [50], but the absence of new diffraction peaks rules out the formation of Cu<sub>2</sub>O crystals. The metal particle size does not increase after the catalytic process, except for the catalyst with the



Fig. 8. Evolution of (A) FUR conversion, (B) FOL yield and (C) MF yield, as a function of Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO. Experimental conditions:  $m_{cat} = 150 \text{ mg}$ , T = 210 °C, H<sub>2</sub> flow = 10 mL min<sup>-1</sup>, feed flow = 2.3 mmol FUR h<sup>-1</sup>.



Temperature (°C)

Fig. 9. Influence of the reaction temperature in the FUR hydrogenation for K-15Cu catalyst. Experimental conditions:  $T_{Red} = 300$  °C,  $m_{cat} = 150$  mg,  $H_2$  flow = 10 mL min<sup>-1</sup>, feed flow = 2.3 mmol FUR h<sup>-1</sup>.



Fig. 10. Influence of the reaction temperature in the FUR hydrogenation for K-15CuCe catalyst. Experimental conditions:  $T_{Red} = 230$  °C,  $m_{cat} = 150$  mg,  $H_2$  flow = 10 mL min<sup>-1</sup>, feed flow = 2.3 mmol FUR h<sup>-1</sup>.

highest Cu-content (K-30Cu), whose particle size increases from 23 to 35 nm after 5 h of TOS.

Concerning the XPS characterization of the used catalysts, the Cu 2p core level spectra reveal that copper species continue being in a reduced

state (Fig. 12). The Cu<sub>LMM</sub> core level signal also show two contributions ascribed to the coexistence of Cu<sup>0</sup> and Cu<sup>+</sup> species, but contribution of Cu<sup>+</sup> signal increases in all cases. This fact indicates the partial surface oxidation of metallic sites, which could be attributed to the formation of H<sub>2</sub>O as by-product in the FOL hydrogenolysis to MF. In the case of the promoted Cu-based catalysts, the surface oxidation of Cu<sup>0</sup> to Cu<sup>+</sup> is lower, which can be explained by their lower selectivity toward MF, thus minimizing the formation of water. It is no clear the role of the Cu<sup>+</sup> in the FUR hydrogenation since some authors have pointed out that Cu<sup>+</sup> species lack catalytic activity [53]. However other authors have pointed out that Cu<sup>0</sup> species acts as a promoter to Cu<sup>+</sup>, being necessary a synergetic effect to obtain the best catalytic conditions [54,55], while other authors have stablished that Cu-species partially or completely reduced have involved in low temperature hydrogenation reactions [56]. On the other hand, the presence of Cu<sup>+</sup> species can also generate Lewis acid sites, which could attract easier the carbonyl group of the furfural molecule the first step of hydrogenation by a side-bond interaction  $\eta^{1}$ -(O)-aldehvde configuration [57]. In any case, it seems clear that oxidation of Cu0 species is not a key factor in the catalytic deactivation. In fact, both K-15CuCe and K-15CuZn also show the presence of higher proportion of Cu<sup>+</sup> species after the catalytic process, although these catalysts hardly carried out the hydrogenolysis reaction of the FOL to MF. In this sense, Natesakhawat et al. pointed out that the amount of Cu<sup>+</sup> species, which could be produced from the oxidation of Cu metal by a low concentration of water vapor, is not appreciable enough to be detected by XPS-Auger [58]. In the same way, Wang et al. established that it is necessary a concentration of 9 mol% H<sub>2</sub>O to detect the presence of Cu<sub>2</sub>O in the bulk and on the surface of Cu/ZnO catalysts so it is expected that the amount of Cu<sup>+</sup> species is likely originated from sample handling instead of a oxidation of Cu<sup>0</sup> during the catalytic reaction [59]

The atomic concentration values indicate a clear increase of the surface carbon content (Table 3), suggesting that catalyst deactivation must be ascribed to the formation of carbonaceous deposits. In this sense, previous research has pointed out that both FUR and FOL interacts strongly with the active sites [16,50], while the interaction of MF with the metallic sites is practically negligible, although higher reaction temperature favors the formation of MF, which can lead to the formation of coke or FUR polymerization [53]. Catalysts with lower Cu content display higher surface carbon contents (65.3 and 69.3% for K-5Cu and K-10Cu, respectively), which decrease for lower copper loadings (41.3–56.5%). Considering the metallic surface, shown in Table 2, the K-5Cu catalyst should reach the maximum FUR conversion value since this catalyst shows the highest metallic surface; however, K-5Cu catalyst is not the most active. In this sense, the XPS analysis of the K-



Fig. 11. XRD patterns of: (A) Cu-based kerolite clays with different copper content and (B) Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO, after 5 h of TOS at 210 °C.



Fig. 12. (A) Cu<sub>LMM</sub> Auger signal of the Cu-based kerolitic clay with different copper content after 5 h of TOS at 210 °C. (B) Cu<sub>LMM</sub> Auger signal of Cu-based kerolitic clay modified with CeO<sub>2</sub> and ZnO, after 5 h of TOS at 210 °C.

5Cu catalyst after the catalytic test shows how this catalyst displays the highest proportion of carbon content located on the surface after the catalytic tests probably due to the clay mineral interacts strongly with the aldehyde and hydroxyl groups of FUR and FOL, respectively by electrostatic interaction through hydrogen bonds. The incorporation of higher Cu-content partially covers the silanol groups that can interact with the reagents and/products so the carbon deposition on the surface of the catalyst diminishes. In fact, Table 3 reports that Cu/ (Si + Al + Mg) increases after the catalytic tests, so the carbonaceous deposits have a higher preference for the surface of the clay mineral in comparison to the metallic sites.

The study of the promotion effect has demonstrated the positive influence of ZnO or  $CeO_2$  addition, since lower surface carbon content are deposited. This fact could be ascribed to the decrease of the hydrogenating capacity of active sites due to their interaction with these promoters, which seem to modify the electronic density in such a way that formation of MF is unfavored. This lower hydrogenation activity minimizes the deposition of carbonaceous species, responsible of the catalyst deactivation (Table 3). On the other hand, the Ce 3d core level spectrum hardly suffers modification (Supplementary Information

Fig. 1), which suggest that Ce4 + species is not reduced during the catalytic test.

The analysis of the carbonaceous deposits by XPS reveals the presence of three contributions in all cases. The main contribution is located at 284.8 eV, and it is assigned to C–C bonds, typical of adventitious carbon, whereas those at 287.0 and 288.3 eV would reveal the coexistence of C–OH, C–O–C and C=O bonds, and O=C=O bonds, respectively [16]. Considering the high concentration of carbon on the surface, it can be concluded that the deactivation of the active phase must be ascribed to the deposition of FUR, polymerized FUR or FOL instead of the oxidation of the Cu<sup>0</sup> sites along the TOS.

# 5. Conclusions

A disordered kerolitic clay formed by kerolite/stevensite mixed layer was used as catalytic support to disperse Cu-species, which were incorporated by the precipitation-deposition method. In all cases, the size of the Cu-crystals is relatively low, reaching crystals with a size lower of 24 nm in all cases. This fact together with the high surface area of the kerolitic clay due to its disorder leads to catalytic systems with high metallic surface, i.e. high proportion of available metal sites.

The catalytic behavior of the Cu-based catalysts supported on kerolitic clay was evaluated in the furfural reaction in gas phase. The catalytic data showed that the furfural conversion is directly related with the Cu content, reaching the maximum values above 85% from a 15 wt.% Cu. In all cases, furfuryl alcohol and 2-methylfuran were the only detected products. The FOL/MF selectivity ratio values show that catalysts with intermediate copper loadings are slightly more selective to 2-methylfuran, whereas the use of a higher copper loading tends to favor the formation of furfuryl alcohol. In any case, the K-xCu catalysts lack selectivity toward a specific compound in any of the catalysts. On the other hand, it is noticeable that all catalysts are relatively resistant to the loss of available Cu-sites by carbonaceous deposits or sintering.

The addition of Ce and Zn oxides of promoters provokes a decrease of furfural conversion in comparison to the K-xCu catalysts. However, the most noteworthy is related with the selectivity pattern, since the incorporation of ZnO, and mainly  $CeO_2$ , modifies the electronic density of the active phase and almost full selectivity to furfuryl alcohol is reached, with a maximum furfuryl alcohol yield close to 80% for K-15Cu (Cu/Ce = 1) catalyst, at 190 °C, after 5 h of TOS.

#### Acknowledgements

The authors are grateful to financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2015-64226-C03-03-R project), Junta de Andalucía (RNM-1565) and FEDER funds.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.06.001.

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