EFFECT OF COOPER ON THE CATALYTIC ACTIVITY FOR ACETYLACETATE COMBUSTION OF $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$ AND $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$ PEROVSKITE-TYPE OXIDES

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(Received: April 22, 2013 - Accepted: July 12, 2013)

ABSTRACT

The effect of lower Cu ($\leq 30\%$) substitution on alkaline earth zirconate ($\text{A}_{1-x}\text{Cu}_x\text{ZrO}_3$; A=Ca, Sr) perovskites prepared via a citrate route and calcined at 700°C has been investigated as catalysts for total acetyl acetate combustion. The thermal behaviour indicates a beneficial effect of Cu in order to decrease the decomposition temperature of Ca and Sr zirconates. The characterization of the solids by atomic absorption spectroscopy (AAS), BET area, SEM, XRD, O_2 -DTP and TPR indicates for the Sr series presence crystalline CuO phase in the copper strontium zirconates, meanwhile almost highly dispersed CuO is detected in the Ca series. Two effects explain the increases in the total acetylacetate combustion of Ca and Sr zirconates upon copper content. For one hand, in the Ca series, highly dispersed CuO phase, easier to be reduced increases the catalytic activity, meanwhile for the Sr series, a large extent of oxygen vacancies explains the catalytic effect.

Keywords: zirconate, calcium, strontium, copper, perovskites, acetyl acetate.

INTRODUCTION

Catalytic oxidation is one of the most important technologies used for the destruction of volatile organic compounds (VOCs) especially when the VOC concentration is low [1-3]. Noble metals supported on alumina are among the most used metal based catalysts [4-6], even though due to their lower cost, the use of mixed metal oxides and perovskites has received great attention [7-9]. Perovskites can be represented by the general formula ABO_3 and the number of potentially interesting perovskites as catalysts is very great, due to the number of A and B cations that can enter into this structure [10]. It is well known that in mixed oxides a redox-type mechanism, where the reactant is oxidized by lattice oxygen and the reduced catalyst is subsequently reoxidized by gas phase oxygen is believed to be possible for oxidation reactions [11]. Commonly the A-site metal is usually rare earth metal and the B-site elements of the first row transition metals. Specifically, in the perovskites to be used as catalysts, the A-site is occupied by lanthanum due to their large thermal stability associated with the size of the lanthanide ions [12]. Thus the activity in oxidation and reduction reaction is mainly determined by the transition metal in the B-site. For lanthanum perovskites, the best catalytic performances in catalytic combustion are exhibited by Co, Fe or Mn as B cation [13-15] attributed to oxygen defects [15, 16]. In general, the reported catalytic performance of perovskites for oxidation reactions are $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ systems, even though recently Pecchi et al [17, 18] reported the advantages of the intrinsic activity and resistance to deactivation of $\text{K}^{1+}\text{Nb}^{5+}\text{O}_3$ perovskites on the catalytic soot combustion. In order to a better enlighten of the role of the perovskite type structure in the catalytic performance of new $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ systems and due to the fact that in the current literature there are no reported studies about the assessment of alkaline earth as catalysts for oxidation reactions, in this article the synthesis and characterization of alkaline earth metal zirconates is reported, represented by ZrCaO_3 and ZrSrO_3 . These have never been reported to be used as catalysts in catalytic abatement of hydrocarbons.

In this work, the effect of the earth alkaline substituted by copper on $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$ and $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$ perovskite-type oxides on the structural, redox and catalytic performance for the total combustion of acetylacetate was studied.

EXPERIMENTAL

$\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$ and $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$ ($x_{\text{Cu}}=0.0, 0.05, 0.1, 0.2, 0.3$) perovskites were prepared via the formation of a citrate complexes using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as metal precursors [19]. To eliminate chlorine ions, the resulting amorphous citrate precursor was washed until constant conductivity, dried in an oven and calcined at 700°C for 10 h.

Differential thermal analysis/thermogravimetry (DTA/TG) experiments were performed at a heating rate of 10°Cmin^{-1} up to 1000°C in Netzsch 409 PC apparatus using an Al_2O_3 crucible in 11% O_2/He mixture using a constant sample weight of 40 mg. Absorption atomic spectroscopy (AAS) was performed by means of a model 3100 Perkin Elmer instrument to determine the zirconia, calcium, strontium and copper composition of the bulk. Specific areas were calculated through the BET method from the nitrogen adsorption isotherms at -196°C on a Micromeritics apparatus Model ASAP 2010. X-ray powder diffraction (XRD) patterns were obtained with Ni-filtered $\text{CuK}\alpha_1$ radiation ($\lambda=1.5418\text{\AA}$), using a Rigaku diffractometer. Scanning electron microscopy (SEM) micrographs were obtained in a JEOL model JSM 6380 LV. TPR and oxygen TPD experiments were performed in a TPR/TPD 2900 Micromeritics system with a thermal conductivity detector. For the TPR experiments, the reducing gas was a mixture of 5% H_2/Ar ($40\text{ cm}^3\text{min}^{-1}$) and a heating rate of 10°Cmin^{-1} . For the TPD experiments the samples were exposed to oxygen for 1 h at 700°C , following by cooling to room temperature in the same atmosphere. After switching the atmosphere to a helium flow, the sample was heated at a constant rate of 10°Cmin^{-1} and the oxygen desorbed was monitored with a thermal conductivity detector. The catalytic activity in the total combustion of acetyl acetate was performed in a conventional flow reactor at atmospheric pressure. In each experiment, 300 mg of catalysts diluted with 100 mg of silica as an inert were used. The activity was measured at different temperatures. The reactant mixture was fed into the reactor at 150 mLmin^{-1} and the temperature lineally increased up to 150°C and maintained constant for 30 min. Then, it was raised to a new isothermal temperature using the same heating rate (1°Cmin^{-1}). Several isothermal steps were performed until reaching complete conversion. The used reactant gaseous mixture was $\text{C}_4\text{H}_8\text{O}_2/\text{O}_2/\text{He}=1:8:91$ (molar). Reactor effluents were analysed using an on-line gas chromatograph Hewlett Packard model HP 4890D with thermal conductivity detector that works at a temperature of 150°C and a current of 150mA. The column used was a 30-m capillary Supelco 25462. The carrier gas (He) flow through the column was 4 mL min^{-1} and the injector temperature at 150°C . A Quadrupole Mass Spectrometer Shimadzu, GCMS-QP5050 model was used to detect small traces of products.

RESULTS AND DISCUSSION

The TG/DTG-MS follow-up of the calcination process as well as the evolution of the 14, 18, 28, 32, 44 and 46 amu masses were followed by mass spectrometry (MS). Figures 1.a) and 1.b) show the DTG profiles of the Ca and Sr zirconates precursors. In the DTA profiles (not shown) a first wide endothermic peak between 50 and 300°C related with the evaporation of

adsorbed water and decomposition of the citrate group [20] was detected. These decompositions can be individualized in the DTG profiles of Figure 1, in which the first peak $\sim 100^\circ\text{C}$ corresponds to water and the second at $\sim 260^\circ\text{C}$ to the organic group. A second large exothermic peak between 420°C and 450°C is attributed to the formation of stable carbonates $\text{Sr}_2\text{Zr}_2\text{O}_3\text{CO}_3$ and $\text{Ca}_2\text{Zr}_2\text{O}_3\text{CO}_3$ [19] which is decomposed after 5 h of calcination at 650°C to the crystalline SrZrO_3 and CaZrO_3 structure. This exothermic peak is also detected in the large loss weight of the DTG profiles of Figure 1 between 400°C and 430°C stables and intermediates carbonates with varying mole ratios of $\text{Ca}:\text{Zr}:\text{CO}_3$ and $\text{Sr}:\text{Zr}:\text{CO}_3$ at $\sim 450^\circ\text{C}$ [19]. The TG-MS experiments (results not shown) indicates that for larger Cu contents ($x_{\text{Cu}}=0.10; 0.20; 0.30$) H_2O and CO_2 were the only evolutes gases, meanwhile for copper free and the lowest copper content ($x_{\text{Cu}}=0.0; 0.05$), evolution of CO was also detected in a minor content. The obtained results indicate a beneficial effect of Cu in order to decrease the decomposition temperature of Ca and Sr zirconates.

Figure 1. DTG profiles. 1.a) $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$; 1.b) $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$

Table 1 summarises the Ca, Sr and Cu content determined by AAS. The satisfactory agreement between experimentally and nominal contents, specially for Cu content indicates almost no weight loss of metals during the synthesis.

The XRD pattern of the zirconates calcined at 700°C are shown in Figures 2.a) and 2.b). The diffractograms of Ca series in Figure 2.a) indicate a mixture of

crystalline non-stoichiometric $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ (26-341) and stoichiometric CaZrO_3 (35-645) perovskite structure. The triplet centered at 31.53° is characteristic of an orthorhombic system [20]. Only CuO (48-1548) as segregated phase is seen at larger Cu content, even though it can be also present highly dispersed at lower Cu content. For the Sr series, the diffraction lines in Figure 2.b) indicates that pure SrZrO_3 corresponds to an orthorhombic perovskite structure SrZrO_3 (70-283) and upon Cu substitution large amount of segregated phases identified as CuO (48-1548), ZrO_2 (37-31) and traces of CuSrO_3 (46-22) even at lower substitution degree were detected. For the higher Cu content, the planes observed at 2θ 23-26 and $65-70$ degree corresponds to ZrCu (49-148). The crystallite sizes, calculated by means of the Scherrer method through the XRD profiles are listed in Table 1. A lower effect in the crystallite size upon copper substitution is detected in the Ca series (39 to 42 nm) compared with the Sr series (30 to 42 nm) allowing to assume that the segregated phases in the Sr series should be in a higher crystalline phase. The different intensities in the diffraction peak of CuO in the Ca and Sr series makes possible to believe that highly dispersed CuO phase or in a less crystalline structure may be present in the Ca series, meanwhile a more crystalline CuO phase is present in all of the studied copper strontium zirconates.

Figure 2. X-ray diffraction patterns. 2.a) $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$; 2.b) $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$

The BET surface area values are shown in Table 1. The obtained values, larger than the reported in the literature for other perovskites-type structure [11] can be attributed to agglomerated and compact structures, as it is observed in the SEM micrographs. The Ca series shows closer S_{BET} values upon Cu substitution, meanwhile, large differences were obtained in the Sr series and follow the general trend of a decrease in the crystallite size with the S_{BET} values. The decrease in the specific area with the increases of Cu content can be attributed to a lower dispersion degree of the segregated phases.

Table 1. Bulk composition (wt%), crystallite size by DRX, grain size by SEM, surface area and amount of oxygen desorbed (DTP-O₂) for Ca and Sr zirconates.

	Ca or Sr ^{a,b}	Cu ^{a,b}	d _{hkl} , nm	d _{SEM} , nm	S _{BET} , m ² g ⁻¹	DTP-O ₂ , μmolm ⁻²
CaZrO ₃	20.0 (22.4)	0.0 (0.0)	39	230	19	0.30
Ca _{0.95} Cu _{0.05} ZrO ₃	18.1 (21.1)	1.7 (1.8)	42	320	14	0.23
Ca _{0.9} Cu _{0.1} ZrO ₃	17.3 (19.9)	2.9 (3.5)	42	210	16	0.22
Ca _{0.8} Cu _{0.2} ZrO ₃	15.0 (17.4)	6.8 (6.9)	39	170	17	0.20
Ca _{0.7} Cu _{0.3} ZrO ₃	13.5 (15.1)	11.0 (10.0)	41	160	15	0.30
SrZrO ₃	36.8 (38.6)	0.0 (0.0)	30	400	22	0.00
Sr _{0.95} Cu _{0.05} ZrO ₃	34.6 (36.9)	1.3 (1.4)	44	550	10	0.10
Sr _{0.9} Cu _{0.1} ZrO ₃	36.8 (35.1)	2.3 (2.8)	42	560	11	0.12
Sr _{0.8} Cu _{0.2} ZrO ₃	29.8 (31.6)	5.5 (5.3)	26	430	12	0.18
Sr _{0.7} Cu _{0.3} ZrO ₃	26.9 (27.9)	9.5 (8.7)	27	300	15	0.23

^aEstimated error is below 5%; ^bNominal values are in parentheses

Particle size and morphology of the calcined powders were examined by scanning electron microscopy (SEM). Figures 3.a) and 3.b) shows the micrographs of two representative solids, the ones with 10% of Cu content for the Ca and Sr series. A narrower particle size distribution with an average around 100-200 nm can be seen, much larger than their crystallite size measured by XRD, indicative that the solid are aggregated as polycrystals. Energy Dispersive Analysis X-ray (EDAX) was carried out to quantify the O/Zr, Cu/Zr and (Ca or Sr)/Zr ratios of the solid composition. Since perovskite-type oxides are crystalline structures, an increase in the nominal ratio must be enriched due to the presence of segregated phases, not detected by XRD patterns if they are highly dispersed. Although EDAX is not a surface sensitive technique, the obtained atomic ratio, an average of more than 30 EDAX analyses, can provide information about the dependence on these ratios upon the copper substitution [21]. Table 2 displays the O/Zr, alkaline earth (Ca or Sr)/Zr and Cu/Zr EDAX ratios. The O/Zr ratio of 10, larger than the nominal of 3, indicates an oxygen excess with no dependence upon xCu substitution. Due to the limitations of the technique and the small differences in the metallic contents, the discussion is focused only on the observed tendencies. For Ca series lower Ca/Zr EDAX ratios than the nominal are observed, meanwhile, the Sr/Zr ratios are larger than the nominal. As AAS analysis indicates no loss of Ca, Sr and Cu, this result must be related to copper dispersion or insertion into the perovskite structure. This issue will be subsequently discussed.

Figure 3.a)

Figure 3.b)

Figure 3. SEM micrographs. 3.a) Ca_{0.9}Cu_{0.1}ZrO₃; 3.b) Sr_{0.9}Cu_{0.1}ZrO₃

It is well known the importance of the evolution of oxygen during temperature programmed desorption experiments that deal with the redox properties of the perovskites. Figures 4.a) and 4.b) presents the experimental oxygen TPD profiles. For Ca series, the profiles are the expected for perovskites type oxides [14, 22]. Basically the first desorption peak at temperatures lower than 100°C corresponds to the physisorbed oxygen species and the second peak, which clearly appears for the non stoichiometric copper free Ca_{0.15}Zr_{0.8}O_{1.85} perovskite at 250°C, is attributed to the so-called a-oxygen, ascribed to oxygen vacancies that desorbs below 500°C. The presence of a-oxygen in Ca_{0.15}Zr_{0.8}O_{1.85} is an expected result due to the intrinsic oxygen vacancies of a non stoichiometric solid. Upon copper substitution, this peak appears only as a shoulder with virtually the same intensity for all of the Ca series. For the higher copper content, a last desorption peak started at 500°C, corresponds to the so-called b-oxygen associated with the lattice oxygen[23] or with oxygen species related to the redox properties of the solid. This peak, not finished at 700°C clearly appears for the higher Cu content, and its presence can be correlated to the insertion of copper into the perovskite structure. TPD – MS experiments confirm that the evolved gas and the He flow only contain oxygen. The amount of desorbed oxygen was measured by deconvolution of the oxygen desorption curves using a Lorentzian peak shapes in a computer peak-fitting routine. As listed in Table 1, the amount of desorbed oxygen with copper content increases only in the Sr series. Regarding to the Cu free zirconates, the non-stoichiometric Ca_{0.15}Zr_{0.8}O_{1.85} perovskite structure explain the large extent

of a-oxygen compared with SrZrO_3 . In the stoichiometric pure SrZrO_3 perovskite, with no oxygen vacancies, the effect of copper increases the oxygen mobility, being larger for the highest Cu content. Therefore, a large effect in the formation of oxygen vacancies upon copper content is obtained in the Sr series. Meanwhile, in the non stoichiometric pure $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ perovskite with large extent of oxygen vacancies, almost no changes with copper content was detected.

Table 2. EDAX ratios (nominal in parentheses), ignition temperature and apparent activation energy for Ca and Sr zirconates.

	O/Zr	Ca/Zr	Sr/Zr	Cu/Zr	$T_{50}, ^\circ\text{C}$	Eact app, kJmol^{-1}
CaZrO_3	10 (3)	0.7 (1.0)	--	0.0 (0.0)	450	164
$\text{Ca}_{0.95}\text{Cu}_{0.05}\text{ZrO}_3$	10 (3)	0.7 (0.95)	--	0.1 (0.05)	303	159
$\text{Ca}_{0.9}\text{Cu}_{0.1}\text{ZrO}_3$	10 (3)	0.7 (0.9)	--	0.1 (0.1)	302	163
$\text{Ca}_{0.8}\text{Cu}_{0.2}\text{ZrO}_3$	11 (3)	0.6 (0.8)	--	0.2 (0.2)	296	101
$\text{Ca}_{0.7}\text{Cu}_{0.3}\text{ZrO}_3$	10 (3)	0.6 (0.7)	--	0.2 (0.3)	298	106
SrZrO_3	11 (3)	--	1.2 (1.0)	0.0 (0.0)	378	170
$\text{Sr}_{0.95}\text{Cu}_{0.05}\text{ZrO}_3$	10 (3)	--	1.0(0.95)	0.1 (0.05)	305	129
$\text{Sr}_{0.9}\text{Cu}_{0.1}\text{ZrO}_3$	10 (3)	--	1.0 (0.9)	0.2 (0.1)	308	128
$\text{Sr}_{0.8}\text{Cu}_{0.2}\text{ZrO}_3$	11 (3)	--	1.2 (0.8)	0.3 (0.2)	308	130
$\text{Sr}_{0.7}\text{Cu}_{0.3}\text{ZrO}_3$	10 (3)	--	1.1 (0.7)	0.4 (0.3)	306	132

Figure 4. Oxygen profiles spectra. 4.a) $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$; 4.b) $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$

The TPR profiles shown in Figures 5.a) and 5.b) indicates that the copper free zirconates show no reduction peak, indicative of a non-reducible system, similar to LaFeO_3 [24, 25]. Upon copper addition, a larger effect in the reducibility is detected in the Ca series, compared to the Sr zirconates.

In Ca series, for $x\text{Cu}=0.05$ only one well defined reduction peak is seen and two or more reduction peaks appears for the $x\text{Cu}\geq 0.1$ perovskites. The single and well-defined reduction peak at 230°C is attributed to the reduction of well dispersed CuO phase and the wider second reduction peak to a more crystalline CuO phase [26, 27]. The TPR of the Sr series show almost no reducibility at lower copper content ($x\text{Cu}\leq 0.1$). Only for the larger copper content some reduction peaks appear. Considering that XRD indicates presence of crystalline CuO even at lower copper content, this means that in the Sr series, the CuO could be partially inserted into the perovskite structure or in a high crystalline phase. These results indicate large reducibility upon copper content in the Ca series with a large extent of highly dispersed CuO phase.

The catalytic activity of the zirconates was measured in the total acetyl acetate oxidation in a flow reactor using an excess of oxygen. Prior to the reaction measurements, diffusion control assays were carried out in order to assure kinetic regime conditions. Carbon dioxide, water, acetaldehyde and CO were the detected products. The experimental curves of acetylacetate conversion, showed in Figures 6.a) and 6.b), correspond to the typical sigmoidal curves in which the reaction starts at about 200°C and reaches total conversion at temperatures lower than 400°C . The ignition temperature (T_{50}) is defined as the temperature required to obtain a 50% of conversion and the apparent activation energy is indicated in Table 2. Considering that T_{50} for the non catalyzed reaction is 520°C the studied solid show catalytic activity (decrease of T_{50}) in the studied reaction that increases upon Cu content. The apparent activation energy displays the same trend, a decrease upon copper substitution, indicative of the benefit effect of copper in the catalytic activity of the studied Ca and Sr zirconates. It is well known that in catalytic oxidation reactions using perovskites as catalysts, at lower temperatures the catalytically active species are electrophilic oxygen species and at higher reaction temperatures the oxidation proceeds under participation of nucleophilic lattice oxygen species via the Mars van Krevelen mechanism[28]. Although these redox-type mechanisms are widely accepted, the experimental verification is not easy due to the formation of oxygen vacancies or lattice oxygen occurs in parallel with textural and structural changes of the solid.

The characterization results indicate almost no insertion of copper into the perovskite structure. It is likely that the similarity of the ionic radius of Cu^{2+} (0.073 nm) and Zr^{4+} (0.072 nm) both in a 6-fold coordination allows the substitution of copper by zirconia instead of the larger earth alkaline Ca^{2+} (0.112 nm) and Sr^{2+} (0.124 nm) both in an 8-fold coordination. Moreover, in heterogeneous catalysis, the catalytic activity of mixed oxides can be related to the high mobility of oxygen species and/or high dispersion of metallic phases. It is believed that the catalytic activity of the studied copper substituted Ca or Sr zirconates can be related to highly dispersed CuO phase,

catalytically more active than a crystalline CuO phase [29, 30] and the presence of oxygen vacancies. These means, that the catalysts with highly dispersed CuO phase, easier to be reduced will have higher catalytic activity. From the characterization results, in the Ca series the addition of copper do not increase in a large extent the large oxygen mobility of the non stoichiometric pure $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ perovskite, whereas the reducibility of the solid is clearly increased. This means that the highly disperse CuO phase present in the Ca series is easier to be reduced. The X-ray diffraction lines also indicate CuO in a high dispersion degree for the Ca series and the lower EDAX Ca/Zr ratios is a consequence of the covered of Ca by the highly CuO segregated phase. With regard to the Sr series the addition of copper increases both, the reducibility and in a large extent the oxygen mobility of the stoichiometric pure SrZrO_3 perovskite. The large extent of segregated phases detected by DRX and the Sr/Zr EDAX ratios higher than the stoichiometric indicates a lower dispersion of CuO and the sharper X-ray diffraction lines indicate higher crystallinity of the CuO phases.

Figure 5. Temperature-programmed reduction profiles. 5.a) $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$; 5.b) $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$.

The effect of the copper addition in the catalytic behaviour of the Ca zirconates can be explained on the basis of a highly dispersed CuO phase, easier to be reduced catalytically more active than the crystalline CuO phase. On the other hand, for the Sr zirconates, the increase in the catalytic activity is explained by the effect of higher oxygen mobility upon copper substitution. It is noticeable the high catalytic activity (low T_{50}) of the pure CaZrO_3 and SrZrO_3 a stoichiometric perovskite, almost non reducible solid compared to pure. This non expected result is in line with the higher catalytic activity of a non-reducible perovskite as LaFeO_3 compared to LaCoO_3 and points out the specific properties of perovskite-type oxides to be used as catalysts for a given oxidation reaction [16, 31, 32].

Figure 6. Stationary-state acetylacetone conversion. 6.a) $\text{Ca}_{1-x}\text{Cu}_x\text{ZrO}_3$; 6.b) $\text{Sr}_{1-x}\text{Cu}_x\text{ZrO}_3$. (---) non catalyzed; (x) $x\text{Cu}=0.0$; (▲) $x\text{Cu}=0.05$; (■) $x\text{Cu}=0.1$; (●) $x\text{Cu}=0.2$; (▼) $x\text{Cu}=0.3$.

CONCLUSIONS

The changes in the catalytic activity in the acetyl acetate combustion of Ca and Sr zirconates as a result of copper content can be correlated with the chemical composition and the active surface oxygen species. For one hand, in the Ca series, highly dispersed CuO phase easier to be reduced, meanwhile for the Sr series, the large extent of oxygen vacancies explains the increases of the catalytic effect.

ACKNOWLEDGEMENTS

The authors thank CONICYT-Fondecyt Grant 1130005 for financial support.

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