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Novel hierarchical Co₃O₄/ZnO mixtures by dry nanodispersion and their catalytic application in the carbonylation of glycerol

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ABSTRACT

Cobalt oxide nanoparticles (40–50 nm) were hierarchically dispersed on ZnO microparticles (0.2–1 μ m) using a low-energy dry mixing method, resulting in a zinc–cobalt interaction that stabilizes Co²⁺ sites. Raman spectroscopy is used to evidence the nature of the interphase reaction between ZnO and Co₃O₄ particles. The system evolves toward the formation of the spinel phase, ZnCo₂O₄, with further temperature thermal treatment at 400 °C. The catalytic activity of these materials was tested in the transformation of renewable materials via the carbonylation of glycerol by urea. Room-temperature-prepared Co₃O₄/ZnO systems exhibit catalytic behavior in the production of glycerol carbonate reaching conversions up to 69% in 4 h with close to 100% selectivity.

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1. Introduction

Glycerol is a renewable strategic raw chemical, which use depends on its efficient conversion to value-added products. However, glycerol exhibits a too versatile chemistry, resulting in a broad distribution of products that typically hampers its application [1–4]. The use of co-reactants to narrow product distribution is a particularly successful approach; for instance, the use of ammonia to make acrylonitrile, both in the vapor phase and in the liquid phase, results in yield values to acrylonitrile of 40% with nearly 90% selectivity [5-7]. Like acrylonitrile, glycerol carbonate is also a valuable chemical. Glycerol carbonate is one of the glycerol derivatives that attract more scientific and industrial interest due to its potential end uses. The search for successful routes to efficiently produce glycerol carbonate from renewable raw materials is a key subject for different manufacturing areas since these may compete and replace petroleum-derived materials [8-10]. CO₂ has been used as a carbonylating agent under supercritical conditions [11]; but its experimental conditions are highly demanding. Other carbonylating agents like dimethyl carbonate [12,13], dialkyl carbonates [14] or urea [15] allow for milder reaction conditions. Urea is a particularly attractive carbonylating

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agent; Mouloungui et al. [15] patented the synthesis of glycerol carbonate by carbonylation of glycerol with urea over heterogeneous zinc catalysts such as zinc sulfate, zinc organosulfate and zinc ion exchange resins. Calcined ZnSO₄ affords the best results by reaction with urea (glycerol carbonate yields 86% in 2 h) at 150 °C and 40 mbar; the ammonia formed is removed during reaction. However, ZnSO₄ salt is soluble in glycerol; thus, this is a homogeneous catalysis reaction, where the catalyst is partially recovered after reaction. There is a strong strategic and environmental benefit in developing a heterogeneous catalyst for this process. Heterogeneous catalysts are particularly efficient for cabonylation of glycerol with urea [16,17] affording good yield values under more moderate reaction conditions. Climent et al. [17] have recently reported the carbonylation of glycerol (glycerol carbonate yield 72% in 5 h) with urea at 145 °C over heterogeneous catalysts such as basic oxides (MgO and CaO) and mixed oxides (Al/Mg and Al/Li) derived from hydrotalcites with adequate acid-base pairs [17].

The reactions described above have a significant environmental and sustainable value; the development of environmental friendly catalytic process requires heterogeneous catalysts. The preparation stage is a key component in the environmental value of a catalyst. We have reported a residue-free and solvent-free preparation method to make hierarchical nanoscaled catalysts dispersed on microscaled particles [18,19]. This nanodispersion method opens up opportunities to obtain hierarchical nanoparticles-microparticles

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systems with unusual properties by mixing oxides of dissimilar materials. The interfaces created after the partial reaction of two oxides exhibits new and interesting properties due to proximity and diffusion phenomena [20,21], which become relevant at the nanoscale range. We have demonstrated that interface-related properties lead to the appearance of ferrimagnetism in mixtures of ZnO and Co_3O_4 despite the constituting oxides present diamagnetic and paramagnetic characters at room temperature, respectively [22,23].

The effects in the preparation procedure of Co_3O_4/ZnO mixtures obtained by dry nanodispersion is presented and discussed. In addition, the effects on the phase structure and morphology of Co_3O_4/ZnO mixtures are evaluated. It is shown that Co_3O_4/ZnO interface properties are modified producing changes in the catalytic properties of the mixtures as it was tested in the carbonylation reaction of glycerol with urea.

2. Experimental details

2.1. Nanodispersion procedure of Co₃O₄/ZnO mixtures

The compositions with 0.5, 1, 5 and 10 wt.% of Co_3O_4 nanoparticles (hereafter, named as ZCo0.5-Nps, ZCo1-Nps, ZCo5-Nps and ZCo10-Nps respectively) were prepared by incorporating the appropriate amounts of Co_3O_4 nanoparticles and ZnO microparticles by a previously described dry nanodispersion procedure [18]. The dry dispersion process consisted on shaking Co_3O_4 /ZnO mixtures and 1 mm ZrO₂ balls in a 60 cm³ nylon container for 5 min at 50 rpm using a tubular-type mixer. Pure ZnO and Co_3O_4 powders were also subject to the same mixing process to ensure that no structural disorder contributions were produced by the mixing process. The raw materials used in this study are cobalt oxide (Co_3O_4 , 99.99%) and ZnO (99.99%). Analytical grade powders were dried at 110 °C for 2 h before dry mixing.

2.2. Morphology characterization

The particle size and morphology of the powders were evaluated using secondary electrons images of Field Emission-Scanning Electron Microscopy, FE-SEM (Hitachi S-4700) and Transmission Electron Microscopy (TEM, Hitachi H-7100 175) with an accelerating voltage of 120 kV. For TEM investigations, powders were suspended in isopropanol, and a drop of this suspension was deposited on a holey carbon-coated film supported on a 400 mesh copper grid.

2.3. Structural characterization

The crystalline structure was determined by X-ray diffraction analysis (XRD, Siemens D5000, Munich, Germany, Cu K α radiation). The Raman spectra were measured in air atmosphere at room temperature, using the 514 nm excitation line from an Ar⁺ laser operating at 10 mW. The signal was collected by a microscope Raman spectrometer (Renishaw Micro-Raman System 1000) in the 100 cm⁻¹-1100 cm⁻¹ range.

2.4. Reaction procedure in the carbonylation of glycerol with urea

In a typical experiment, an equimolecular mixture of glycerol and urea were placed in a 10 mL round-bottom flask in a batch reactor for 5 min before the catalyst was added. The reaction was heated in an oil bath at 140–145 °C and stirred at 300 rpm. Reactions were run in the absence of a solvent at atmospheric pressure removing ammonia from the system by air passing through the reactor. The amount of catalyst used was 6% by weight of the initial amount of glycerol. After the reaction was completed, water was added and the catalyst was removed by filtration. The catalyst was washed with acetone several times and dried at room temperature for 24 h to be used in a new cycle of reaction. The reactions were followed by gas chromatography using a HP5890 gas chromatograph (GC) equipped with a 50-m-long Ultra2–5% Phenyl methyl siloxane capillary column and a flame ionization detector (FID) (Accuracy <5% relative).

3. Results and discussion

3.1. Morphology of the Co₃O₄/ZnO mixtures

Fig. 1a and b shows the morphology of pure ZnO and Co₃O₄ raw materials. The FE-SEM micrograph, Fig. 1a, shows the typical ZnO morphology, consisting mainly of elongated prismatic particles and nearly cubical particles, with sizes of 0.2-1.0 µm and an average particle size 0.5 μ m. The morphology of Co₃O₄ particles is that of small spherical particles with sizes of 40-50 nm (see insert Fig. 1b) which form globular agglomerates ranged from 0.5 μ m to $4 \mu m$, Fig. 1b. On the other hand, the FE-SEM image of the mixture of ZnO with 10 wt.% of Co₃O₄ nanoparticles prepared by dry nanodispersion method is shown in Fig. 1c. The micrographs show that most of the Co_3O_4 agglomerates disappear and the individual nanoparticles are adhered to the ZnO surfaces Fig. 1d. The dispersion and great adherence of nanoparticles could indicate the appearance of Co₃O₄/ZnO interfaces at room temperature between these materials, due to the high initial reactivity of the Co₃O₄ and ZnO. All individual nanoparticles are dispersed below 10 wt.% Co_3O_4 , but some agglomerates become apparent at higher Co_3O_4 loadings. This means that a dispersion limit of Co₃O₄ nanoparticles on ZnO microparticles has been reached. It is worth to mention that ZnO particles morphology is kept invariant, as a result of the low energy of the mixture process. The TEM micrograph in Fig. 1d confirms the presence of interfaces between ZnO-Co₃O₄ after the dry mixing process.

3.2. Structural characterization of Co₃O₄/ZnO system

The X-ray diffraction patterns of the raw materials and the Co_3O_4/ZnO mixtures, displayed in Fig. 2, can be indexed on the basis of a phase mixture constituted by a majority of ZnO and a minority of Co_3O_4 . As expected, the intensity of the diffraction peaks of Co_3O_4 phase becomes increasingly stronger with Co_3O_4 loading.

In order to check the effect of the thermal treatment temperature on the phase structure, the mixtures were thermally treated at 500 °C for 36 h. No changes are observed in the XRD pattern after such thermal treatment, Fig. 2.

No evidence of metallic Co, CoO or any additional phases different than ZnO, Co₃O₄ were found in any sample, within the XRD resolution. The expected reaction between Co₃O₄ and ZnO is the formation of a Zn_{1-x}Co_xO wurtzite-type solid solution, which possesses the same lattice parameters than ZnO. This would explain the fact that only the diffraction peaks of ZnO are observed at 500 °C. There is little difference between the ionic radii of Co²⁺ (0.058 nm) and Zn²⁺ (0.060 nm) and, therefore, small changes in the *c*-axis value due to Co substitution in ZnO can be expected. At higher temperatures, the formation of the spinel phase ZnCo₂O₄ is possible but this phase is isostructural with Co₃O₄ and X-ray diffraction patterns cannot determine whether the spinel forms.

The Co₃O₄/ZnO mixtures prepared by nanodispersion method and thermally treated at 500 °C have also been investigated by Raman spectroscopy, and the resulting spectra are depicted in Fig. 3a. ZnO has a wurtzite structure, with two formulae per primitive cell



Fig. 1. Field emission-scanning electron microscopy micrograph of the initial materials: (a) ZnO microparticles and (b) Co_3O_4 nanoparticles agglomerates. The insert shows a detail of Co_3O_4 spherical nanoparticles by Transmission Electron Microscopy. FE-SEM micrograph of ZnO particles covered by Co_3O_4 nanoparticles adhered to the surface after low-energy mixing. (c) Mixture of ZnO with 10 wt.% of Co_3O_4 nanoparticles. (d) TEM micrograph detail of the Co_3O_4 nanoparticles dispersed over ZnO elongated prismatic particles observed in the mixtures with Co_3O_4 contains higher than 5 wt.%.



Fig. 2. XRD patterns corresponding to the raw materials, the Co_3O_4/ZnO mixtures and thermally treated at 500 °C during 36 h as a function of the Co_3O_4 content.

with $C_{3\upsilon}$ symmetry. For this structure, the group theory predicts the following Raman active modes $A_1 + E_1 + 2E_2$ [24,25]. These distinct Raman active modes of ZnO can be observed in Table 1 along with their proposed assignment. Moreover, Table 1 also identifies the main Raman modes of Co₃O₄, which Raman spectra can be observed in Fig. 3a. Considering that spinel structures belong to the Fd3m (O_h⁷) space group, one should theoretically expect five Raman active modes $(A_{1g} + E_g + 3F_{2g})$. Pure cobalt oxide exhibits the five expected Raman active modes in this spectral range: A_{1g} (689 cm⁻¹); F_{2g} (619, 521 and 191 cm⁻¹) and E_g (481 cm⁻¹). The high-frequency peak, A_{1g} , has been assigned to vibrations involving the motion of oxygen atoms inside the octahedral unit (e.g. CoO_6 in Co₃O₄). Their breadth is related to the cation-anion bond lengths and polyhedral distortion occurring in the spinel lattice [26] whereas F_{2g} and E_g modes combine the vibration of tetrahedral (e.g. CoO₄ in Co₃O₄) and octahedral sites [27]. The Raman spectra of the ZnO and Co₃O₄ as raw materials and the Co₃O₄/ZnO mixtures, displayed in Fig. 3a, can be indexed on the basis of a phase mixture constituted by both phases. After annealing the $Co_3O_4/$ ZnO mixtures at 500 °C, the cobalt oxide Raman bands present changes. The possible insertion of Zn²⁺ into the lattice of spinel slightly alters the observed vibrations frequencies as shown in Fig. 3b. Raman bands are substantially blueshifted. The Raman peak associated with the motion of oxygen atoms inside the octahedral unit, A_{1g} , in the Co₃O₄ is the most intense for any annealing time. Moreover, the nanodispersion of Co₃O₄ produces a slight broadening of the A_{1g} Raman peak and the appearance of a double peak upon treatments at ~500 °C. The second peak could be attributed to the appearance of the spinel phase $ZnCo_2O_4$ at ${\sim}714\,cm^{-1}$ which emerges concomitantly, Fig. 3b. Actually, at Co₃O₄ concentration as low as 0.5 wt.%, the formation of the ZnCo₂O₄ spinel is clearly observed. The formation of the spinel requires a large diffusion of Zn atoms (not only those at the particle surface) and therefore is more favored by the longer annealing time. Recently, the formation of the spinel phase at low temperature, \sim 400 °C, was reported for this system [28], which could be related to zinc cations diffusion.



Fig. 3. (a) The Raman spectra of raw materials, Co_3O_4/ZnO mixtures and thermally treated at 500 °C during 36 h as a function of the Co_3O_4 content. (b) Magnified Raman spectra in the wavenumber ranges from 640 to 760 cm⁻¹ of the Co_3O_4/ZnO mixtures thermally treated and Lorentzian fits of the individual peak of the Raman mode associated with the appearance of the spinel phase ($ZnCo_2O_4$).

Table 1

Main Raman modes observed on ZnO and Co_3O_4 phases. The intensity of the peaks is marked from very low to very intense. (1: low; m: medium; s: strong; v: very).

| References |
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| [26,27] |
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In summary, Raman spectroscopy uncovers a progressive interface reaction in ZnO–Co₃O₄ mixtures, which is produced by the dry dispersion method in which cobalt oxide nanoparticles are effectively dispersed onto ZnO microparticles. Longer annealing treatments at low temperature allow Zn cations to diffuse and form the spinel phase, ZnCo₂O₄. Zn cations are active at temperatures near 400 °C due to the thermal desorption of interstitial Zinc (Zn_i⁺) and the formation of oxygen vacancies (V_{o})_s. This behavior facilitates Zn cations volatilization from the wurtzite crystal lattice and the zinc diffusion in nearest particles of dissimilar materials, thus promoting the solid-state reaction during the thermal treatment [22,29].

3.3. Catalytic activity of the Co₃O₄/ZnO system

According to previous works, urea reacts with glycerol when heated in the presence of a catalyst; the reaction mechanism follows four possible steps: (I) carbamylation of glycerol to glycerol urethane (A), (II) carbamylation of glycerol urethane to glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) (B) with abstraction of the ammonia or (III) carbonylation of glycerol urethane to 5-(hydroxymethyl)oxazolidin-2-one (C) without abstraction of the ammonia and (IV) glycerol carbonate can react with another molecule of urea to obtain (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (D), which would decrease glycerol carbonate selectivity [15,17], see Scheme 1.

Fig. 4 shows the activity results obtained during carbonylation of glycerol over the constituting oxides and the Co₂O₄/ZnO catalytic systems prepared by dry nanodispersion at room temperature and those further calcined at 500 °C. ZnO is hardly more active than the blank test, in line with literature data [30]. Co₃O₄ is more active and selective. The combination of both oxides exhibits a catalytic activity that depends on the specific preparation procedure and treatment temperature. Cobalt oxide loading in Co₃O₄/ZnO increases the activity dramatically for the room-temperature series but it exhibits a moderate increase for the series calcined at 500 °C (Fig. 4). Thus, the catalytic activity is hampered upon calcination. The room-temperature series with 1%wt Co₃O₄ exhibits 100% selectivity to glycerol carbonate, but it is only slightly more active than the blank test; at higher loading (10 wt.% Co₃O₄), conversion reaches 69% with 97% selectivity to glycerol carbonate. The performance of this series is unlike those reported earlier [17], where total conversion is attained with selectivity values near 75%. For the Co₃O₄/ZnO series, calcination at 500 °C has a deleterious effect on both conversion and selectivity.

When Co_3O_4 nanoparticles disperse on ZnO microparticles, the Co_3O_4/ZnO systems were catalytically active since the nanodispersion method of preparation leaves the Co_3O_4 active sites dispersed in the Co_3O_4/ZnO system. After calcination of the Co_3O_4/ZnO systems, the phenomenon can be explained as follows: ZnO may interact with Co_3O_4 and form inactive species such as $ZnCo_2O_4$ spinel, as confirmed by Raman spectroscopy, decreasing the number of free active sites Co_3O_4 in the system. The zinc–cobalt oxide spinel has very little activity, because of the restriction of the active species of cobalt in the tetrahedral sites. A further increase in the amount of cobalt oxide (from 1 to 10 wt.%) leads to an increase in the catalytic activity, which is less significant for calcined



Scheme 1. Reaction mechanism between glycerol and urea. Reaction products: (A) Glycerol urethane; (B) Glycerol Carbonate; (C) 5-(hydroxymethyl)oxazolidin-2-one; (D) (2-oxo-1,3-dioxolan-4-yl)methyl carbamate.



Fig. 4. Catalytic performance of Co_3O_4/ZnO catalytic systems for the synthesis of glycerol carbonate at 145 °C during 4 h.

samples since the spinel is the main phase present in the system. Finally, the Co_3O_4/ZnO catalytic system was found to be completely recoverable and reusable at least three times without any loss in activity and selectivity during the carbonylation of glycerol.

To conclude the Co_3O_4/ZnO systems prepared by dry nanodispersion at room temperature showed the best results compared with raw materials and those other Co_3O_4/ZnO systems preheated at 500 °C. Particularly, the samples containing more Co_3O_4 (10 wt.%) exhibited better activity (up to 69% conversion, 97% selectivity to glycerol carbonate) demonstrating that a good dispersion of the Co_3O_4 catalytically active sites in the interface of the system that play a crucial role during reaction. The results shown highlighting the importance of the synthesis method used in the preparation of this heterogeneous catalytic system.

The phenomenology described here can be interpreted as a simple model based on the formation of Co_3O_4/ZnO interfaces at room temperature and the formation of new crystalline phases, $ZnCo_2O_4$, at low thermal treatment, see Fig. 5. Fig. 5a and b shows a schematic representation of an individual ZnO particles hierarchically coated with Co_3O_4 nanoparticles by the dry nanodispersion method. The dispersion and great adherence of nanoparticles may indicate that a spontaneous reaction occurs at room temperature between these materials, due to the high initial reactivity of the



Fig. 5. Schematic of the attachment of nanoparticles to the outer surface of an individual ZnO microparticle obtained by dry nanodispersion method, (a) Co_3O_4/ZnO mixtures before and (b) after of the dry nanodispersion process. (c) Magnified ZnO surface cover Co_3O_4 nanoparticles hierarchically dispersed, where it can be observed Co_3O_4 –ZnO interfaces. (d) Schematic representation of the spinel phase formed after thermal treated at 500 °C/36 h.

Co₃O₄ and ZnO [19]. Fig. 5c shows the magnification of the ZnO surface, which illustrates the formation of new interfaces between ZnO microparticles and Co₃O₄ nanoparticles. The dry nanodispersion process performed to mix ZnO and Co₃O₄ creates new reactive surfaces (as evidenced by FE-SEM and TEM) that must favor the catalytic activity. This novel way to de-agglomerate nanoparticles has been applied in the carbonylation reaction of glycerol with urea producing novel properties at the interfaces with a high activity and selectivity catalytic. The high reactivity of ZnO may promote a higher availability of Zn cations to diffuse into Co₃O₄ nanoparticles, and thus the stable spinel phase is rapidly formed when the Co₃O₄/ZnO were thermally treated at 500 °C during 36 h as it can be observed in Fig. 5d. The thermal treatment provokes the formation of inactive species such as ZnCo₂O₄ spinel decreasing the number of free active sites Co_3O_4 in the system and therefore presented a lower catalytic activity.

4. Conclusions

This work presents the preparation of hierarchical nanoscaled Co_3O_4/ZnO catalytic systems using a very fast, easy and ecofriendly (no solvent, no surfactant, no residue) dry nanodispersion method of synthesis. This room-temperature preparation method results in a clear interaction between Co_3O_4 and ZnO oxides, endowing them with high activity (69% conversion and near 100% selectivity) for the transformation of renewable materials as the carbonylation of glycerol by urea at moderate reaction conditions (140 °C/4 h). The methodology here proposed offers invaluable insight into catalysts design and for their mass production due its simplicity.

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References

 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. Ed. 46 (2007) 4434.

- [2] R.R. Soares, D.A. Simonetti, J.A. Dumesic, Angew. Chem. Int. Ed. 45 (2006) 3982.
- [3] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Eur. J. Lipid Sci. Technol. 111 (2009) 788.
- [4] M. O Guerrero-Pérez, J.M. Rosas, J. Bedia, J. Rodríguez-Mirasol, T. Cordero, Recent Patents Chem. Eng. 2 (2009) 11.
- [5] M.O. Guerrero-Pérez, M.A. Bañares, ChemSusChem. 1 (2008) 511, doi:10.1002/ cssc.200800023.
- [6] V. Calvino-Casilda, M.O. Guerrero-Pérez, M.A. Bañares, Green Chem. 11 (2009) 939.
- [7] V. Calvino-Casilda, M.O. Guerrero- Pérez, M.A. Bañares, Appl. Catal. B: Environ. 95 (2010) 192.
- [8] J.H. Teles, N. Rieber, W. Harder, US Patent 5 359 094, 1994.
- [9] J.R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodríguez, C. Ramírez-López, L. Lorenzo-Ibarreta, J. Torrecilla-Soria, M.C. Villarán-Velasco, App. Catal. A: Gen. 366 (2009).
- [10] C. Vieville, J.W. Yoo, S. Pelet, Z. Mouloungui, Catal. Lett. 56 (1998) 245.
- [11] M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, J. Mol. Catal. A: Chem. 257 (2006) 149.
- [12] J. Ochoa-Gómez, Olga Gómez-Jiménez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodríguez, C. Ramírez-López, L. Lorenzo-Ibarreta, J. Torrecilla-Soria, M.C. Villarán-Velasco, Appl. Catal. A: Gen. 366 (2009) 315.
- [13] Z. Herseczki, T. Varga, G. Marton, Int. J. Chem. Reactor Eng. 7 (2009) A87.
- [14] A. Takagaki, K. Iwatani, S. Nishimura, K. Ebitani, Green Chem. 12 (2010) 578.
- [15] S. Claude, Z. Mouloungui, J.-W. Yoo, A. Gaset, US Patent 6025504, 2000.
- [16] M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, J. Catal. 268 (2009) 106.
- [17] M.J. Climent, A. Corma, P. de Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, J. Catal. 269 (2010) 140.
- [18] J.F. Fernández, I. Lorite, F. Rubio-Marcos, J.J. Romero, M.A. García, A. Quesada, M.S. Martín-González, J.L. Costa-Krämer, Patent Numbers WO2010010220-A1; ES2332079-A1, 2010, to Consejo Superior de Investigaciones Científicas, CSIC.
- [19] M.S. Martín-González, M.A. García, I. Lorite, J.L. Costa-Krämer, F. Rubio-Marcos, N. Carmona, J.F. Fernández, J. Electrochem. Soc. 157 (2010) E31–E35.
- [20] A. Brinkman, M. Huijben, M. Van Zalk, J. Huijben, U. Zeitler, J.C. Maan, W.G. Van der Wiel, G. Rijnders, D.H.A. Blank, H. Hilgenkamp, Nature Mater. 6 (2007) 493.
- [21] F.Y. Bruno, J. Garcia-Barriocal, M. Torija, A. Rivera, Z. Sefrioui, C. Leighton, C. Leon, J. Santamaria, Appl. Phys. Lett. 92 (2008) 082106.
- [22] A. Quesada, M.A. García, M. Andrés, A. Hernando, J.F. Fernández, A.C. Caballero, M.S. Martín-González, F. Briones, J. Appl. Phys. 100 (2006) 113909.
- [23] M.S. Martín-González, J.F. Fernández, F. Rubio-Marcos, I. Lorite, J.L. Costa-Krämer, A. Quesada, M.A. Bañares, J.L.G. Fierro, J. Appl. Phys. 103 (2008) 083905.
- [24] R. Cuscó, E. Alarcón-Lladó, J. Ibáñez, L. Artús, J. Jiménez, B. Wang, M.J. Callahan, Phys Rev. B 75 (2007) 165202.
- [25] C.A. Arguello, D.L. Rousseau, S.P.S. Porto, Phys. Rev. 181 (1969) 1351.
- [26] S.Z.V. Marinkovic, N. Romecevic, Sci. Direct 27 (2007) 903.
- [27] C.F. Windisch, G.J. Exarhos, K.F. Ferris, M.H. Engelhard, D.C. Stewart, Thin Solid Films 45 (2001) 398.
- [28] M. Peiteado, S. Sturm, A.C. Caballero, D. Makovec, J. Ceram. Soc. Jpn. 118 (2010) 337.
- [29] F. Rubio-Marcos, A. Quesada, M.A. García, M.A. Bañares, J.L. García Fierro, M.S. Martín-González, J.L. Costa-Krämer, J.F. Fernández, J. Solid State Chem. 182 (2009) 1211.
- [30] W.M. Shaheen, M.M. Selim, Int. J. Inorg. Mater. 3 (2001) 417.