Deciphering the role of water and zinc-doping process in polyol-based approach for the obtaining of Zn/Co/Al-based spinels: toward "green" mesoporous inorganic pigments

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Electronic supplementary information



Fig. S1. Overlay of the FTIR spectra of water-added $wPZn_xCo_{1-x}Al$ precursors (x = 0, 0.2, 0.4)



Fig. S2. Overlay of the FTIR spectra of water free $PZn_xCo_{1-x}Al$ precursors (x = 0, 0.2, 0.4)

For both type of precursors, $wPZn_xCo_{1-x}Al$ dark-blue gels and $PZn_xCo_{1-x}Al$ light-green powders, the presence of the intense and structured bands in the 1750-1500 cm⁻¹ region together with the medium intensity absorption centered at 1420 cm⁻¹ could be attributed to v(C=O) stretching vibration from unreacted acetylacetone as well as from the hydrolisis by-products, acetone or ester. The strong and sharp absorptions from ca. 1100 and 1050 cm⁻¹ and medium intensity bands 3390 cm⁻¹ are specific to v(C-OH) from 1,4-BD. Also, for water-free intermediates, the intense peak from ca. 1107 cm⁻¹ could result from vibration mode of O-H bond in aluminium hydroxide or boehmite that are likely forming together with cobaltaluminum based intermediates. Weak absorptions from ca. 2940 and 2880 cm⁻¹ are attributed to stretching vibrations of C-H bonds from the organic residua. Also, the occurrence of the incipient spinelic phase is visible in FTIR spectra as broad, intense and multistructured absorption cover the 400-800 cm⁻¹. However, the shoulders positions differ depending on the zinc/cobalt ratio and, in some cases, show a superposition of different spinelic phases



Fig. S3. The overlapped NIR-UV-Vis spectra for the precursors obtained in water-assisted synthesis $wPZn_xCo_{1-x}Al$ (x = 0, 0.2, 0.4).



Fig. S4. The overlapped NIR-UV-Vis spectra for precursors obtained in water-free synthesis, $PZn_xCo_{1-x}Al (x = 0, 0.2, 0.4).$

For the precursors obtained in aqueous synthesis, $wPZn_xCo_{1-x}AI$, the NIR-UV-Vis plots have similar shapes and are specific to Co^{II}/Co^{III}-based chromophores. For zinc-free sample (x = 0), the absorptions from visible and NIR region are typical to d-d electronic transitions of Co(II), ${}^{4}A_2(F) \rightarrow {}^{4}T_1(P)$ and ${}^{4}A_2(F) \rightarrow {}^{4}T_1(F)$, respectively. For Zn-doped samples (x = 0.2, 0.4) the visible and near-infrared bands are brodened likely due to an increase of the octahedral Co(III) cations amount and the overlap of d-d electronic transition for $[Co^{II}O_4]_{Td}/[Co^{II}O_6]_{Oh}$ and $[Co^{III}O_6]_{Oh}$ chromophores with ligand to metal charge transfer (LMCT) bands from O²⁻ to Co³⁺ cations. For the series of water free $PZn_xCo_{1-x}AI$ precursors (x = 0, 0.2 and 0.4), UV and visible bands are broad but well-delimited, with typical peaks at ca. 300 and 500 nm. For both series of precursors, the occurrence of the visible and near-infrared bands characteristic to tetrahedral cobalt(II) ions indicate an incipient formation of the cobalt/zinc aluminate phase.



Fig. S5. XRD patterns for water-free $PZn_xCo_{1-x}AI$ (x = 0, 0.2, 0.4) precursors (* indicates the diffraction peaks specific to (020), (120), (031) and (200) planes from γ -AlO(OH) phase).



Fig. S6. PL spectra of water free $PZn_xCo_{1-x}Al$ precursors (x = 0, 0.2, 0.4)



Fig. S7. SEM micrographs of water-free $PZn_xCo_{1-x}Al(x=0)$ precursor showing the cocoonlike morphology of the aggregate of particles at two different magnifications: (a) 1 µm and (b) 3 µm



Fig. S8. SEM micrographs of water-free $PZn_xCo_{1-x}Al$ (x = 0.4) precursor showing the cocoon-like morphology of the aggregate of particles at at different magnifications: (a) 30 μ m; (b) 10 μ m; (c) 5 μ m; (d) 3 μ m and (e) 1 μ m



Fig. S9. EDX spectrum for water-free $PZn_xCo_{1-x}Al$ (x = 0.4) precursor.



Fig. S10. TG, DTG and DSC curves of water-assisted $wPZn_xCo_{1-x}Al (x = 0.2)$ sample.



sample.



Fig. S12. TG, DTG and DSC curves of $wPZn_xCo_{1-x}Al (x = 0.4)$ sample.



sample.





Fig. S14. Results of the Rietveld refinement on the XRD data for $wZn_xCo_{1-x}Al$ (x = 0)



Fig. S15. Results of the Rietveld refinement on the XRD data for $wZn_xCo_{1-x}Al$ (x = 0.2)



Fig. S16. Results of the Rietveld refinement on the XRD data for $wZn_xCo_{1-x}Al$ (x = 0.4)



Fig. S17. Results of the Rietveld refinement on the XRD data for $Zn_xCo_{1-x}Al$ (x = 0)



Fig. S18. Results of the Rietveld refinement on the XRD data for $Zn_xCo_{1-x}Al$ (x = 0.2)



Fig. S19. Results of the Rietveld refinement on the XRD data for $Zn_xCo_{1-x}Al$ (x = 0.4)



Fig. S20. Raman spectra for water-free $Zn_xCo_{1-x}Al$ oxides (x = 0, 0.2, 0.4)



Fig. S21. High-resolution C 1s XPS spectra of from water-assisted $wZn_xCo_{1-x}Al$ (a-c) and $Zn_xCo_{1-x}Al$ (d-f), where x = 0 (a, d), 0.2 (b, e) and 0.4 (c, f).

Fig. S21 exhibits the high-resolution spectra of the C 1s level, showing the same components for all the samples, as the carbon presence on the surface is only due to contamination, most likely resulting from the carbonaceous by-products from hydrolysis process and adsorbed on the oxide surfaces. The sp² and sp³ hybridized carbon was identified at ~284.6 eV and ~285.7 eV (component 1 and 2, respectively), in very small amount oxygen-functionalized carbon C=O, at ~287 eV, or O-C=O, at ~288.8 eV associated with component 3, and at ~290.0 eV, some contaminant carbon associated with CO₂ (component 4).

	C 1s	O 1s	Al 2p	Zn 2p	Co ^{2+/} Co ³⁺ (Co ₃ O ₄)	C0 ²⁺	Co 2p					
wZn _x Co _{1-x} Al												
x = 0	4.6	55.0	25.8	0.0	26.6	73.4	14.6					
x = 0.2	8.4	50.3	29.1	2.2	6.3	93.7	10.0					
x = 0.4	13.3	56.0	21.4	2.7	22.4	77.6	6.5					
$Zn_xCo_{1-x}Al$												
x = 0	7.4	59.6	25.6	0.0	2.1	97.9	7.4					
x = 0.2	5.2	62.3	28.7	0.7	1.3	98.7	3.1					
x = 0.4	9.6	55.9	29.9	1.4	1.3	98.7	3.2					

 Table S1. Results of XPS survey scan given in atomic percentage.

	0		Al	Al		Со		Zn				
	Energy (eV)	Atomic (%)	Energy (eV)	Atomic (%)	Energy (eV)	Atomic (%)	Energy (eV)	Atomic (%)				
wZn _x Co _{1-x} Al												
x = 0	0.52 (Ο Kα1)	57.25	1.49 (Al Kα1) 1.74 (Al Kβ1)	26.96	0.69 (Co Lα1) 0.78 (Co Lβ1) 6.97 (Co Kα1) 7.64 (Co Kβ1)	15.79	-	-				
<i>x</i> = 0.2	0.52 (O Kal)	65.07	1.48 (Al Ka1)	26.54	0.66 (Co Lα1) 0.80 (Co Lβ1) 6.93 (Co Kα1) 7.68 (Co Kβ1)	6.51	0.99 (Zn Lα1) 1.04 (Zn Lβ1) 8.67 (Zn Kα1) 9.62 (Zn Kβ1)	1.88				
<i>x</i> = 0.4	0.52 (Ο Κα1)	51.08	1.48 (Al Kα1)	27.77	0.71 (Co Lα1) 0.80 (Co Lβ1) 6.93 (Co Kα1) 7.62 (Co Kβ1)	13.01	0.95 (Zn Lα1) 1.02 (Zn Lβ1) 8.63 (Zn Kα1) 9.57 (Zn Kβ1)					
				Zn _x Co _{1-x} Al								
x = 0	0.50 (Ο Kα1)	72.07	1.48 (Al Kα1) 1.72 (Al Kβ1)	24.94	0.70 (Co La1) 0.80 (Co Lβ1) 6.98 (Co Ka1) 7.65 (Co Kβ1)	2.99	-	-				
<i>x</i> = 0.2	0.52 (Ο Kα1)	61.72	1.46 (Al Kα1)	35.92	0.69 (Co Lα1) 0.80 (Co Lβ1) 6.96 (Co Kα1) 7.66 (Co Kβ1)	1.88	0.98 (Zn Lα1) 1.02 (Zn Lβ1) 8.63 (Zn Kα1)	0.48				
<i>x</i> = 0.4	0.54 (Ο Kα1)	74.05	1.48 (Al Kal)	24.58	0.69 (Co Lα1) 0.78 (Co Lβ1) 6.93 (Co Kα1) 7.63 (Co Kβ1)	0.82	0.99 (Zn Lα1) 1.05 (Zn Lβ1) 8.63 (Zn Kα1) 9.65 (Zn Kβ1)	0.55				

Table S2. EDX energies (eV) and atomic ratio (%) for water-added $wZn_xCo_{1-x}Al$ and water-free, $Zn_xCo_{1-x}Al$ oxides.



Fig. S22. N₂ adsorption–desorption isotherms of $wZn_xCo_{1-x}Al$ oxide (x = 0) and the corresponding pore size distribution (inset).



Fig. S23. N₂ adsorption–desorption isotherms of $wZn_xCo_{1-x}Al$ oxide (x = 0.2) and the corresponding pore size distribution (inset).



Fig. S24. N₂ adsorption–desorption isotherms of $wZn_xCo_{1-x}Al$ oxide (x = 0.4) and the corresponding pore size distribution (inset).



Fig. S25. N₂ adsorption–desorption isotherms of $Zn_xCo_{1-x}Al$ oxide (x = 0) and corresponding pore size distribution (inset).



Fig. S26. N₂ adsorption–desorption isotherms of $Zn_xCo_{1-x}Al$ oxide (x = 0.2) and the corresponding pore size distribution (inset).



Fig. S27. N₂ adsorption–desorption isotherms of $Zn_xCo_{1-x}Al$ oxide (x = 0.4) and the corresponding pore size distribution (inset).



Fig. S28. Overlay of the FTIR spectra of $wZn_xCo_{1-x}Al$ and $Zn_xCo_{1-x}Al$ oxides (x = 0).



Fig. S29. Overlay of the FTIR spectra of $wZn_xCo_{1-x}Al$ and $Zn_xCo_{1-x}Al$ oxides (x = 0.2).



Fig. S30. Overlay of the FTIR spectra of $wZn_xCo_{1-x}Al$ and $Zn_xCo_{1-x}Al$ oxides (x = 0.4).



Fig. S31. The overlapped NIR-UV-Vis spectra of the $wZn_xCo_{1-x}Al$ oxides (BBEE is band-to-band electron excitation, SFT is spin forbidden transitions and LMCT is ligand to metal charge transfer).



Fig. S32. The overlapped NIR-UV-Vis spectra of the $Zn_xCo_{1-x}Al$ oxides (BBEE is band-to-band electron excitation, SFT is spin forbidden transitions and LMCT is ligand to metal charge transfer).

A comparison of the electronic spectra for both series of oxides, $wZn_xCo_{1-x}Al$ (Fig. S31) and $Zn_xCo_{1-x}Al$ (Fig. S32), reveals significant differences in the UV-Vis region. Thus, the dark-green colored $wZn_xCo_{1-x}Al$ samples (x = 0, 0.2, 0.4) exhibit broad and structured bands covering the region 200-800 nm, with three large shoulders centered at *ca*. 445, 610 and 750 nm. The broad absorptions result from the overlap of the high energy UV (attributed to the fundamental band-to-band electron excitations $O(p) \rightarrow Al(s)/Zn(p)$ and visible absorptions (from $[Co^{II}O_4]_{Td}/[Co^{II}O_6]_{Oh}$ and $[Co^{III}O_6]_{Oh}$ chromophores). Ligand to metal charge transfer absorptions (LMCT) from O^{2-} to octahedral Co^{3+} occur in the 800-550 nm region, whereas LMCT transfer from O^{2-} to tetrahedral Co^{2+} ions are in the 550-300 nm range. The high concentration of Co_3O_4 crystalline phase and, consequently, of the Co^{3+} ions on the octahedral sites determine the dark green color of the calcined oxides.

In the case of blue intense colored $\mathbf{Zn}_x \mathbf{Co}_{1,x} \mathbf{AI}$ oxides, the UV and visible absorptions are well delimited and result from: high energy $O(p) \rightarrow AI^{3+}(s)/Zn_y^{2+}(p)$ band-to-band electron excitations (215-235 nm), LMCT $O^{2-} \rightarrow Co^{2+}(T_d)$ transitions and/or *d-d* forbidden electronic transitions from $Co^{2+}(T_d)$ ions (300-400 nm region). The gradual insertion of Zn^{2+} ions into the spinel lattice determine a slight red shift of the UV bands. Besides, for the richest zinc sample, x = 0.4, the $O(p) \rightarrow AI^{3+}(s)$ and $O(p) \rightarrow Zn^{2+}(p)$ transitions occur as two delimited shoulders at *ca*. 256 and 301 nm, respectively. The visible band with three shoulders at *ca*. 540, 580 and 625 nm gives the intense blue coloration of the $\mathbf{Zn}_x \mathbf{Co}_{1-x} \mathbf{AI}$ oxides. This band could be assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ spin allowed transition for the tetrahedral { $Co^{II}O_4$ } chromophores. The structured pattern of the visible band resulted most likely from the significant effects of the spin-orbit coupling which split the 4T state into three spinor components. The different blue shades of the water-free oxides could be correlated with the zinc/cobalt ratio, particle sizes, as well as the increased concentration of outer aluminum oxide flakes (for x = 0.2, 0.4).

The broad and high intensity absorption from the NIR region (1000-1800 nm) is a common feature of the electronic spectra for both series of oxides (Figs. S31 and S32) and is generally assigned to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$ transition specific to Co²⁺ ions from the tetrahedral sites from spinel lattice. Although the shape of the NIR band is relatively similar for all samples, the more structured band of $\mathbf{Zn}_{x}\mathbf{Co}_{1-x}\mathbf{AI}$ oxides indicates a higher concentration of tetrahedral Co²⁺ ions for which the decrease of T_{d} symmetry, [the ${}^{4}T_{1}(F)$ level is splitted into ${}^{4}A_{2} + {}^{4}B_{1} + {}^{4}B_{2}$ levels and three bands are expected] is visible as three shoulders at *ca*. 1210, 1340 and 1500 nm.



Fig. S33. Schematic representation of the two-step polyol-assisted reaction including pictures of the water-added, $wPZn_xCo_{1-x}Al$, and water free, $PZn_xCo_{1-x}Al$ precursors and their thermolisis products, $wZn_xCo_{1-x}Al$ and $Zn_xCo_{1-x}Al$ oxides.