Electronic Supplementary Information - Synthesis of cobalt aluminate nanopigments by non-aqueous sol-gel route†

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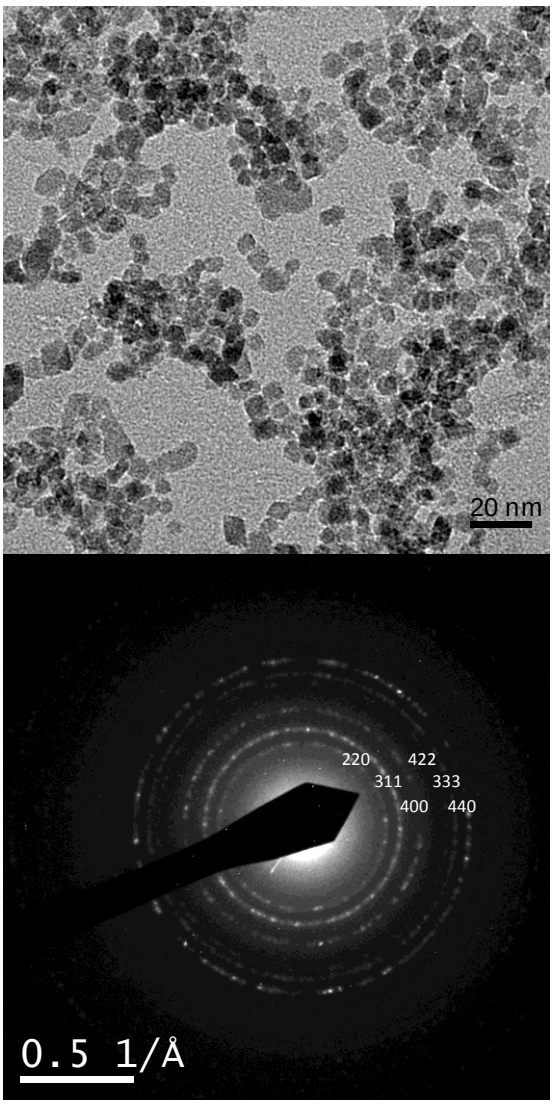

Fig. S1. TEM image of sample 250 ºC and corresponding electron diffraction (ED) pattern showing spots/rings at distances expected for $CoAl_2O_4$.

Table. S1 List of interplanar distances reported for $CoAl_2O_4$ in 40029-ICSD file (d_{REF}), obtained from XRD refinement (d_{XRD}, Fig. 1), ED (d_{ED}, Fig. S1) and from Fourier Transform (d_{FT}, Fig. 2c). dXRD and d_{ED} differ by a constant factor of about 1.05.

hkl	d_{REF}	d_{XRD} (Å)	d_{ED} (Å)	d_{FT} (Å)
220	2.866	2.855	2.73	2.829
311	2.444	2.435	2.33	
400	2.027	2.019	1.92	
422	1.655	1.648	1.58	1.612
333	1.560	1.554	1.48	
440	1.433	1.427	1.36	1.425

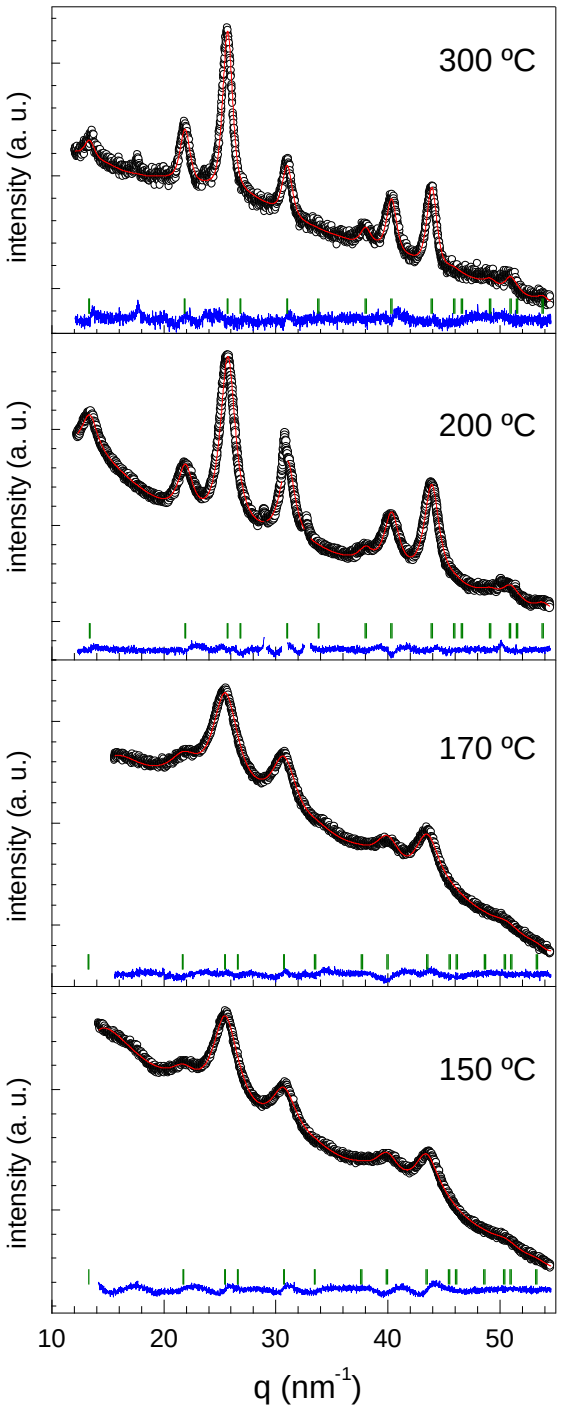

Fig. S2. XRD patterns of cobalt aluminium oxide samples produced at different temperatures. Continuous (red) line corresponds to Rietveld refinement of a spinel (space group Fd-3m) using FullProf software[S1] considering mixed occupancy of tetrahedral and octahedral sites.

Table. S2 - Fitted values of occupancies and corresponding χ^2 values obtained for the cobalt aluminium oxide samples produced at different temperatures. Co, Al and O atomic ratios (%) estimated by EDS. Except for sample obtained at 150 ºC, EDS atomic ratios are close to a Co:Al ratio of 1:2, while Co:O ratio is larger than the 1:4 ratio expected for cobalt aluminium oxide due to the presence of surface water and benzyl alcohol.

sample	*occupancies*	χ^2	*Co/Al/O (%) (EDS)*
300	$^{T}(Co_{0.4}Al_{0.6})\ ^{O}[\ Al_{1.3}Co_{0.7}]\ O_4$	*1.81*	6/13/81
	$^{T}(Co_{0.7})\ ^{O}[\ Al_{2.7}]\ O_4$	*1.83*	
250	$^{T}(Co_{0.43}Al_{0.57})\ ^{O}[\ Al_{1.4}Co_{0.6}]\ O_4$	*2.34*	11/23/66
	$^{T}(Co_{0.7})\ ^{O}[\ Al_{2.3}]\ O_4$	*2.05*	
200	$^{T}(Co_{0.4}Al_{0.3})\ ^{O}[\ Al_{1.7}Co_{0.3}]\ O_4$	*2.14*	-
	$^{T}(Co_{0.5})\ ^{O}[\ Al_{2.3}]\ O_4$	*2.14*	
170	$^{T}(Co_{0.1}Al_{0\cdot6})\ ^{O}[\ Al_{1.2}Co_{0.8}]\ O_4$	*2.49*	*6/11/83*
	$^{T}(Co_{0.4})\ ^{O}[\ Al_{2.9}]\ O_4$	*2.58*	
150	$^{T}(Co_{0.1}Al_{0.8})\ ^{O}[\ Al_{0.9}Co_1]\ O_4$	*3.32*	6/18/76
	$^{T}(Co_{0.5})\ ^{O}[\ Al_{3.2}]\ O_4$	*8.66*	

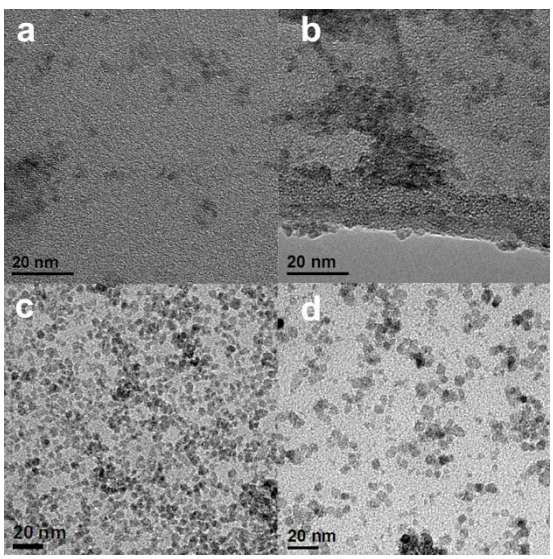

Fig. S3. TEM images of a sample: (a) sample 150 ºC; (b) sample 170 ºC; (c) sample 200 ºC and (d) sample 300 ºC

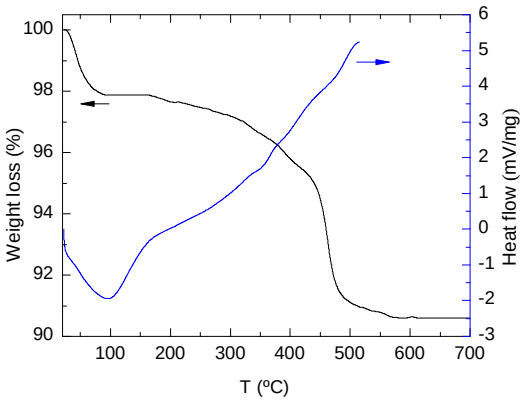

Fig. S4. Thermogravimetric (TGA) and differential scattering calorimetric analysis (DSC) of the transition cobalt-aluminate nanoparticles. The TGA pattern reveals weight losses occurring in tree stage decomposition behaviors. A sharp weight loss occurred in the temperature range 20-100 °C indicating the loss of water molecules; it involves the loss of approximately ≈ 2 % of the original mass. The first endothermic peak at ~100 °C in the DSC curve corresponds to the removal of physisorbed water. The second step, a notable weight loss takes place at temperature between 100-500 °C, is characterized by a sharp/light exothermic peak, it is attributed to the combustion of organic species observed for the sample (like benzyl alcohol that it is known to start to desorbs at around 150 °C).[S2] This combustion process is responsible for a weight loss around 7 %, as may be appreciated in the TG curve. In the last step, weight loss is not much higher; it is due to the residual organic species.

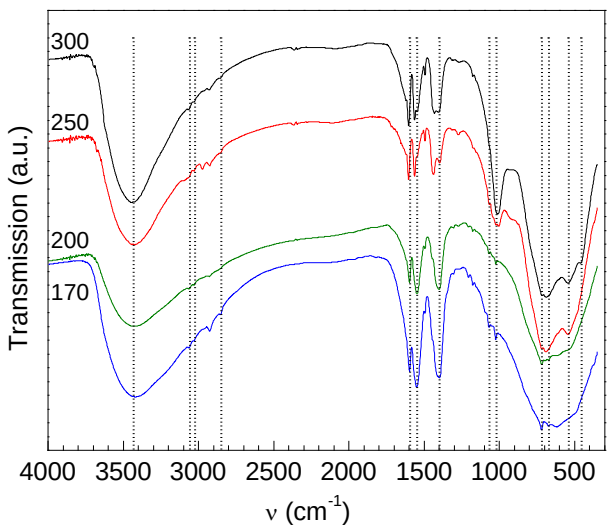

Fig. S5 FT-IR spectra of the $CoAl_2O_4$ nanopowders produced at different temperatures. Vertical lines denote the position of the most relevant absorption bands of sample 170 ºC. A broad adsorption band corresponding to the OH stretching mode appears centered at 3436 cm^{-1}, mainly due to the presence of H_2O and in accordance with TGA findings. The band observed at 3060 cm^{-1} is ascribed to the stretching mode of the CH group of phenyl rings, while the bands between 3026 cm^{-1} and 2853 cm^{-1} region are attributable to the asymmetric and symmetric stretching of

the CH_2 groups, respectively, and the band at 1597 cm^{-1} is assigned to the C=C symmetric stretching in the aromatic rings.[S3]. The bands observed near 1549 cm^{-1} and 1400 cm^{-1} are attributed to asymmetric and symmetric stretching frequencies of carboxylate groups, respectively. The frequency separation of these bands ($\Delta\nu \approx 149$ cm^{-1}) suggests a bridging bidentate interaction[S4] between the carboxylate groups and the metal ions located at the surface of $CoAl_2O_4$. The bands observed at 1069 cm^{-1} and 1025 cm^{-1} are assigned to Al-O-H bending modes.[S5] Their relative intensity increases in samples prepared at 250 ºC and 300 ºC, in accordance with the γ-AlO(OH) impurity observed by XRD.

Finally, the bands observed in the 720 cm^{-1} to 459 cm^{-1} range are associated to metal-oxygen bonds. In particular, the bands at 720 cm^{-1} and 459 cm^{-1} are associated to the stretching and bending modes of (AlO_6), respectively,[S5] while the bands at 675 cm^{-1} and 542 cm^{-1} are assigned to the Co-O and Al-O stretching modes of the $CoAl_2O_4$ nanoparticles.[S6]

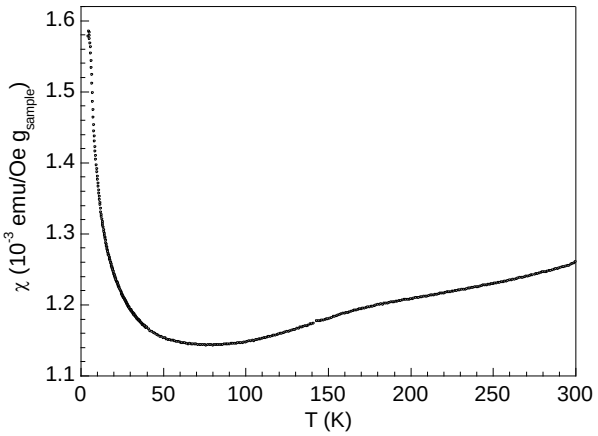

Fig. S6. Temperature dependence of the dc magnetic susceptibility of sample 200 ºC recorded after ZFC procedure.

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