Electronic Supplementary Information

Cupper and Iron co-doping effects on the structural, optical energy band gap, and catalytic behaviour of Co_3O_4 nanocrystals towards low temperature total oxidation of toluene

Hippolyte Todou Assaouka^a, Issah Ngouh Nsangou,^a Manhouli Daawe Daniel^b, Daniel Onana Mevoa^a, Abraham Atour Zigla^b, Patrick Ndouka Ndouka^a, and Patrick Mountapmbeme Kouotou *^{b,c,d}

^aDepartment of Chemistry, Faculty of Sciences, University of Maroua, Maroua P.O. Box 55, Cameroon. ^bNational advanced school of engineering, University of Maroua, P.O. Box. 46, Maroua, Cameroon. ^cAdvanced School of Agriculture, Forestry, Water and Environment, -University of Ebolowa, P.O Box 786 Ebolowa, Cameroon.

^dInstitute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China. *Corresponding authors: <u>mkpatrick1982@gmail.com</u>

Section 1: Catalyst characterization and catalysis text conditions

X-ray Diffraction (XRD) analysis were performed on a Bruker D8. with Cu K α radiation and the XRD data were recorded in the diffraction angles range of 10 to 90° with a scanning rate of 5°/min. The obtained patterns were compared to the JCPDS-ICDD) database as reference to confirm the obtained structure. Additionally, the diameter of NCs was calculated from the most pronounce peaks applaying Scherrer equation (1):

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

Where D refers to the average grains size, k ris the shape factor, λ represent the wavelength, β is the line broadening, and θ is the diffraction angle. The functional groups at the surface of the overall samples were studied by Fourier Transform Infrared (FTIR) spectrometer (Perkin-Elmer), within the wavenumber region of 4000 cm⁻¹ to 400 cm⁻¹, operation with a ramp of 5°C.min⁻¹ under gas flow composed of 5% H₂/O₂ diluted in Ar (0.05 L.min⁻¹). Morphological analysis by Scanning Electron Microscopy (SEM) and the bulk chemical composition analysis using energy dispersive X-ray spectroscopy (EDS) were performed on Hitachi SU 8020 with ultra-high resolution of 1.5 nm (15 kV). X-ray photoelectron spectroscopy (XPS) analysis was employed to evaluate the surface chemical configuration and ionic states of the fabricated NCs. XPS experiment was conducted on Thermo VG ESCALAB250 equipment, operating with 80 eV as transmission energy under 15 kV constant voltage, using an Al K α as excitation source. The concentration of oxygen vacancies (O_V) on the spinel catalyst can be evaluated by the following equation (2): ¹

$$O_V\% = \frac{A_{O_V}}{A_{O_L} + A_{O_V} + A_{O_C}} \times 100\%$$
(2)

Where A_{OV} , A_{OL} and A_{OC} represent the peak area of O^{2-} in surface Ov, lattice oxygen (O_{Lat}), and chemisorbed oxygen (O_{Ads.}), respectively. Temperature-programmed reduction under H₂ flow (H_2-TPR) was performed using Quantachrome NOVA 4200e by the Brunauer–Emmett–Teller (BET). A sample with a mass of 0.05 g was initially pretreated with an Ar stream for 30 min at a fixed temperature of 200 °C to clear away weakly adsorbed surface impurities. UV-visible absorption spectra were measured within the wavenumber ranging from 300 to 900 nm using a UV-visible spectrophotometer (UV-2550, SHIMADZU) and the obtained spectra were used to graphically determined the optical energy bandgap (E_g^{Opt}) using Tauc's equation (3).

$$Ahv = A(hv - E_g)^n \tag{3}$$

Where α stand for the absorption coefficient, A is a constant (refractive index), hu is the photon energy, Eg represent the optical energy bandgap, and n=1/2 for an allowed direct transition.

Catalytic performance measurement

The component of the reaction gas mixture contains 500 ppm C_7H_8 and 20% O_2/Ar , and the total flow was 75 mL/min. The gas hourly space velocity (GHSV) was 22 500 mL g⁻¹ h⁻¹. The concentration of C_7H_8 (500 ppm) in the gas mixture was generated by using an Ar bubbler through a bottle with pure toluene liquid and chilled in an ice–water isothermal bath at 0 °C. All reaction gas lines were heated up to 100 °C by an heating band in order to prevent C_7H_8 condensation on the tube walls. The quantitative analysis of reactants and products were analyzed online at a specific temperature by a gas chromatograph (GC-2014, Shimadu) equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). The C_7H_8 conversion was calculated according to the following equations respectively:

$$X_{C_7H_8} = \frac{[C_7H_8]_{in} - [C_7H_8]_{out}}{[C_7H_8]_{in}} \times 100\%$$
(4)

Where [toluene]in and [toluene]out represents the toluene inlet and outlet.

Moreover, the time-on-stream (TOS) test of the as-prepared NPs was carried out under the same inlet conditions for 30 h continuously constant temperature of 225 $^{\circ}$ C).

Kinetic Measurement

To calculate the apparent activation energies (Ea), we have using the Arrhenius law according to the following equation (5):

$$k = \operatorname{Aexp}^{\left(\frac{E_a}{RT}\right)}$$
(5)

where R is the gas constant (kJ mol⁻¹ K⁻¹); T(K) is the reactor temperature; and A is the preexponential factor.

Section 2: Results and discussion

FTIR analysis of Co₃O₄, Fe₃O₄ and CuO

The FTIR spectrum of Fe₃O₄ shown four main absorption peaks at 555 cm⁻¹, 1366 cm⁻¹, 1607 cm⁻¹ and 3089 cm⁻¹ corresponding to Fe-O stretching mode, H-O-H bending vibration and -OH stretching ² respectively. As for Co₃O₄ the FTIR results exhibit three distinctive bands at 548, 643 and 1298 cm⁻¹ originating from the stretching vibrations of the Co-O and C-O bond respectively. The band at 1584 cm⁻¹ is assigned to the HO vibrations, in excellent agreement with previously reported values in the literature ³. The emission IR spectrum of CuO shows that the bands below 700 cm⁻¹ which correspond to O–H stretching vibration while the other three bands for CuOH vibration modes with a relatively small vibration of H-bond. Again, the strong peaks at around 3252 cm⁻¹ are assigned to the stretching vibration of the OH group of molecular water and of hydrogen-bound OH groups, noting that the peak at 1573cm⁻¹ is due to the bending mode of water molecules. These results is in close agreement with earlier reported CuO nanostructure in the literature ⁴.



Fig. ESM1: FTIR of spinel Co₃O₄, Fe₃O₄ and CuO NPs.

FTIR analysis of Cu_{0.75}Fe_{0.25}Co₂O₄

The FTIR spectra of $Cu_{0.75}Fe_{0.25}Co_2O_4$ display three prominent c emission bands positioned at ~464, ~555 and ~600 cm⁻¹, which are ascribed respectively to Cu–O, Fe–O and Co–O stretching modes of the as-synthesized $Cu_{0.75}Fe_{0.25}Co_2O_4$.⁵ The peak located at ~1198 cm⁻¹ is assigned to C=O symmetric mode. The peaks at ~1495, ~1737 and ~3732 cm⁻¹ correspond to the stretching vibration mode of OH from molecular Cu–OH, Fe–OH and Co–OH ⁶. These observations confirm that no secondary phase was formed, which further supports the XRD result. This finding attest that, no secondary phases were not formed, further supporting the XRD results.



Fig. ESM2: FTIR of Cu_{0.75}Fe_{0.25}Co₂O₄NCs with spinel structure.



Bulk composition: EDS analysis of Co₃O₄, Fe₃O₄ and CuO NPs.

Fig. ESM3. EDS images of the Cu_{0.75}Fe_{0.25}Co₂O₄.



Fig.ESI4. Copper Auger spectra of: (a) CuO and (b) Cu_{0.75}Fe_{0.25}Co₂O₄.

catalysts	Deconvoluted peaks			Peak Area Ratio II/I
-	Peak N ₀ .	Center (°)	Area	
Fe ₃ O ₄	I	280.2	1.01	
		336.7	1.10	
		360.4	1.03	3.21
	II	467.8	3.48	
		515.6	2.84	
		543.9	3.77	
CuO	I	251.7	2.86	
		265.9	3.55	
		273.3	2.95	
	II	-	-	
		-	-	
		-	-	
Co ₃ O ₄		278.4	1.01	
		259.2	1.05	
		250.3	1.15	
	II	378.1	3.87	3.15
		352.3	4.10	
		325.7	2.17	
Cu _{0.75} Fe _{0.25} Co ₂ O ₄	I	171.9	2.20	
		162.8	2.31	
		149.9	2.10	
	II	271.3	3.70	1.70
		245.4	3.95	
		231.1	3.50	

Fable ESI1: H ₂ -TPR quantitative results of Fe ₃ O ₄	, Co_3O_4 , CuO and Cu _{0.75} Fe _{0.25} Co ₂ O ₄ catalysts.
---	---

References

- 1B. Liu, C. Li, G. Zhang, X. Yao, S. S. Chuang and Z. Li, ACS Catal., 2018, 8, 10446–10456.
- 2H. Bai, Y. Zheng, T. Wang and N. Peng, J.Mater. Chem. A, 2016, 4, 14392–14399.
- 3Z.-Y. Tian, N. Bahlawane, V. Vannier and K. Kohse-Höinghaus, *Proc. Combust. Inst.*, 2013, 34, 2261–2268.
- 4G. Kliche and Z. V. Popovic, Phys. Rev. B, 1990, 42, 10060.
- 5A. Askarinejad and A. Morsali, Ultrason. Sonochem., 2009, 16, 124-131.
- 6N. V. Suramwar, S. R. Thakare and N. T. Khaty, Int. J. Nano Dimens., 2012, 3, 75-80.