

Supplementary Materials

Formaldehyde Total Oxidation on Manganese-Doped Hydroxyapatite: The Effect of Mn Content

Dayan Chlala ^{1,2,*}, Jean-Marc Giraudon ¹, Madona Labaki ² and Jean-Francois Lamonier ¹

¹ Unité de Catalyse et Chimie du Solide (UMR 8181-UCCS), University of Lille, CNRS, Centrale Lille, Artois University, F-59000 Lille, France; jean-marc.giraudon@univ-lille.fr (J.-M.G.); jean-francois.lamonier@univ-lille.fr (J.-F.L.)

² Laboratory of Physical Chemistry of Materials (LCPM)/PR2N, Faculty of Sciences, Lebanese University, Fanar, Jdeidet El Metn BP 90656, Lebanon; mlabaki@ul.edu.lb (M.L.)

* Correspondence: dayan.chlala@ul.edu.lb

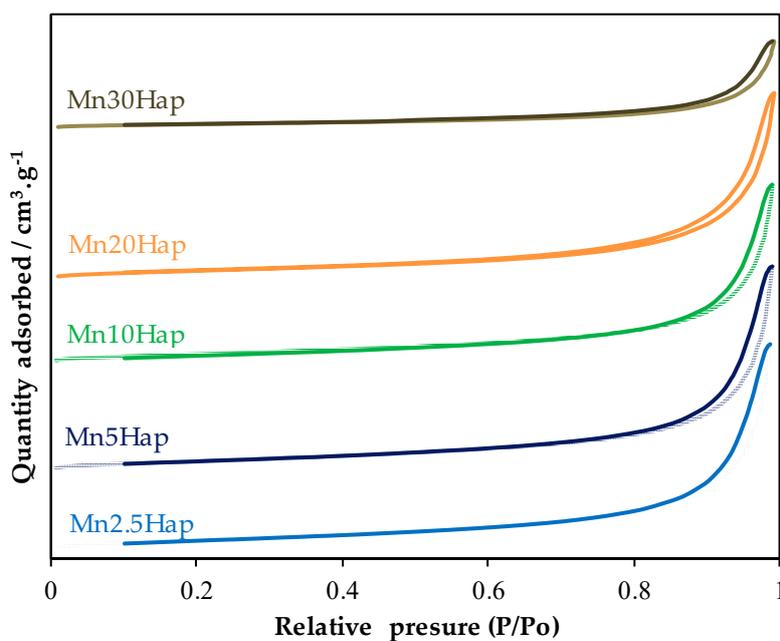
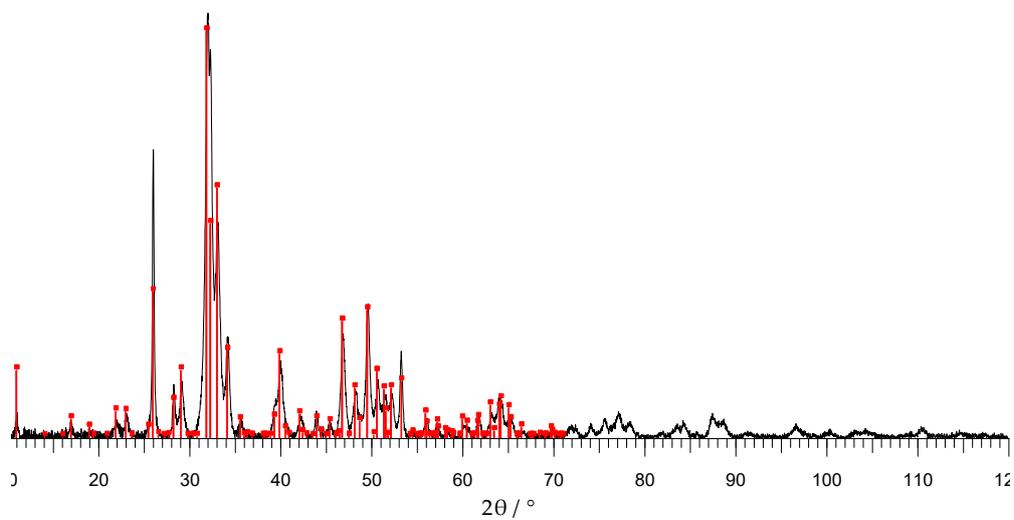
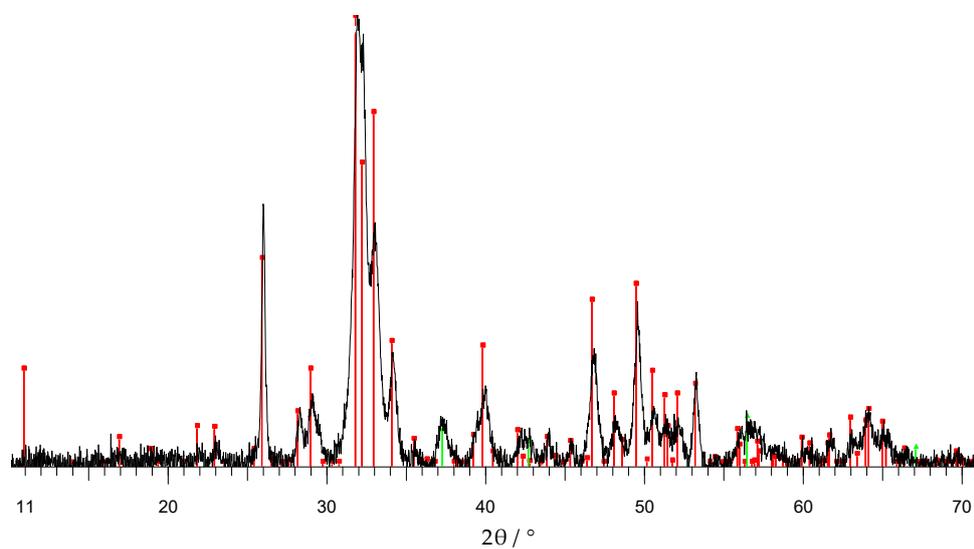


Figure S1. Isotherms of the Mn_xHap samples

a

■ 01-076-0694-Hydroxyapatite- $\text{Ca}_5(\text{PO}_4)_3\text{OH}\cdot\text{Y}$: 126.47%-dx_{dy}:1-WL:1.5406-Monoclinic-a-9.42140-b-18.84280-c-6.88140-alpha 90.000
beta 90.000-gamma 120000-P21/b

b

■ 01-076-0694-Hydroxyapatite- $\text{Ca}_5(\text{PO}_4)_3\text{OH}\cdot\text{Y}$: 126.47%-dx_{dy}:1-WL:1.5406-Monoclinic-a-9.42140-b-18.84280-c-6.88140-alpha 90.000
beta 90.000-gamma 120000-P21/b

▲ 01-089-5171-Akhtenskite-epsilon- $\text{MnO}_2\cdot\text{Y}$: 10.35%-dx_{dy}:1-WL:1.5406-Hexagonal-a-2.79600-b-2.78600-c-4.41200-alpha 90.000
beta 90.000-gamma 120000-P63/mmc

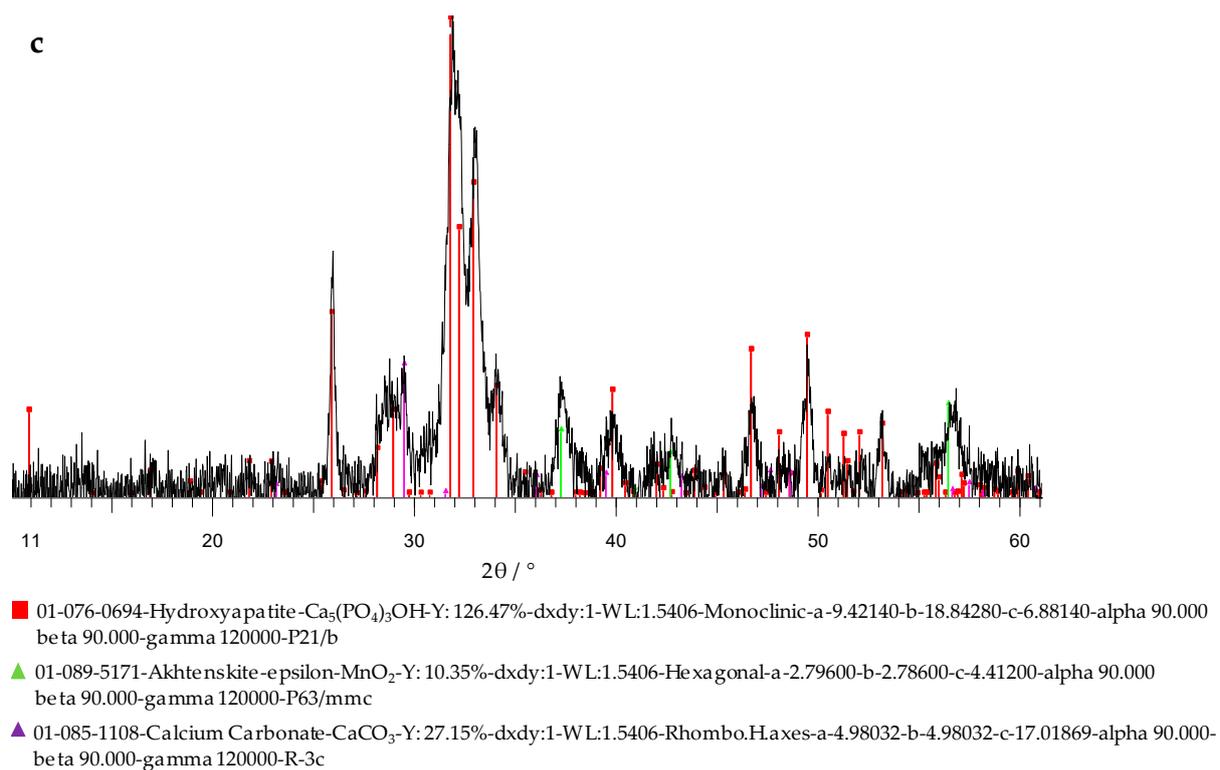


Figure S2. XRD patterns of (a) Mn2.5Hap, (b) Mn20Hap and (c) Mn30Hap.

In-situ Raman spectra were recorded in confocal mode. The 488 nm line of an Ar⁺-ion laser (Melles Griot) was focused through a silica window on the powdered sample (~ 50 mg) placed in the crucible of an environmental chamber (Harrick Scientific) using a 50X long working distance objective (NA: 0.50). The scattered light was collected using the same objective in backscattering configuration, passed through a confocal hole set to 150 μm , dispersed by a 1800 grooves diffraction grating (HORIBA). A Peltier-cooled CCD detector was finally used for spectra collection (Labram HR, HORIBA). Mass flow controllers (Brooks) were used for adjusting the composition of the incoming gas mixture while the total flux was typically set to 30 mL.min⁻¹. The laser power at the sample was 0.75 mW. The procedure applied was the following: After analysis at 30 °C in air and under a mixture of He and O₂ with a He/O₂ molar ratio of 13:5, the solid was heated up to 500 °C in a stepwise manner (heating rate: 5 °C.min⁻¹). Raman spectra were collected under He/O₂ flow every 50 °C while maintaining the temperature constant during spectral acquisition. Subsequent Raman spectra were recorded after a one hour dwell at 500 °C and after cooling down the system to 30 °C. Ambient Raman spectra were recorded using the same spectrometer using a 100X microscope objective (NA: 0.9). The spectral resolution was $\pm 1.5 \text{ cm}^{-1}$. Laser power was 148 μW and acquisition time was about 120 seconds for each scan. The presented spectra were the average of 3 scans.

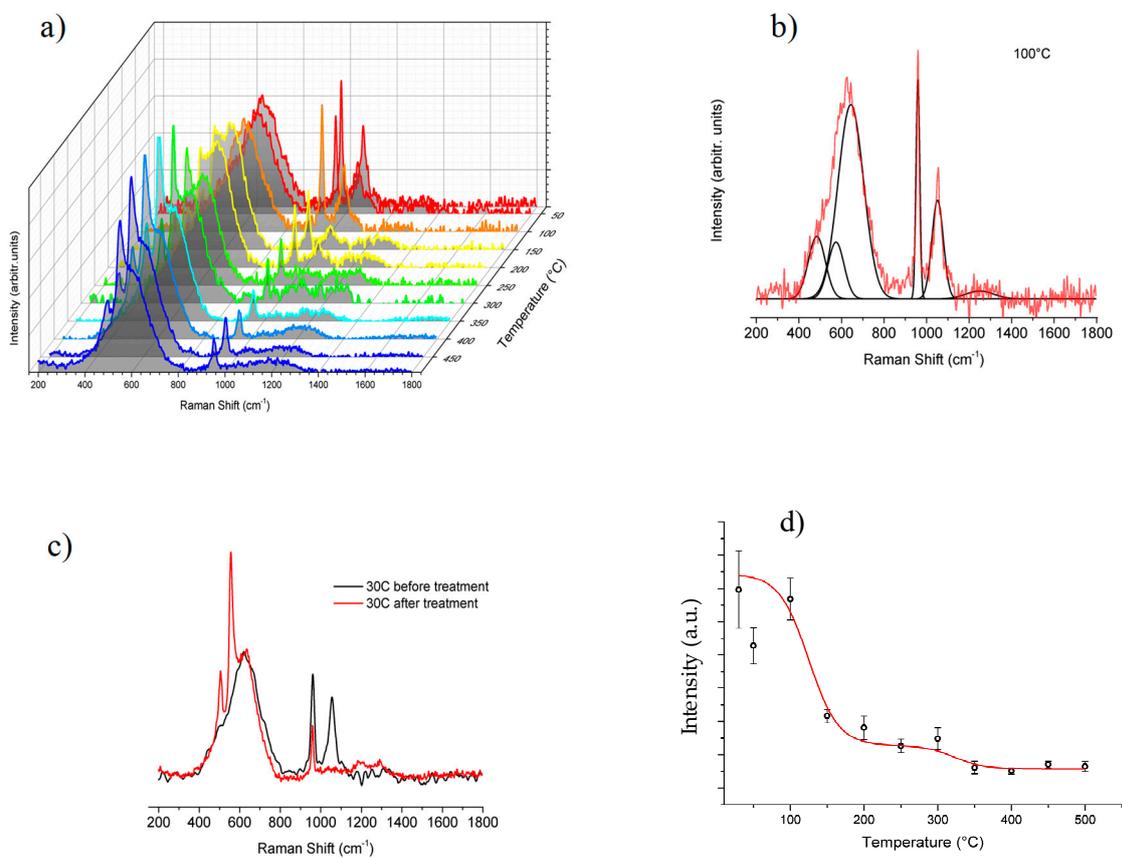


Figure S3. (a) *In situ* Raman spectra as a function of temperature for the precursor of Mn10Hap calcined in 20% O_2 /He atmosphere; (b) Experimental and fitted Raman spectrum at 100°C ; (c) Comparison of the starting and ending Raman spectrum and (d) Monitoring of the intensity of the 1050 cm^{-1} band as a function of temperature.

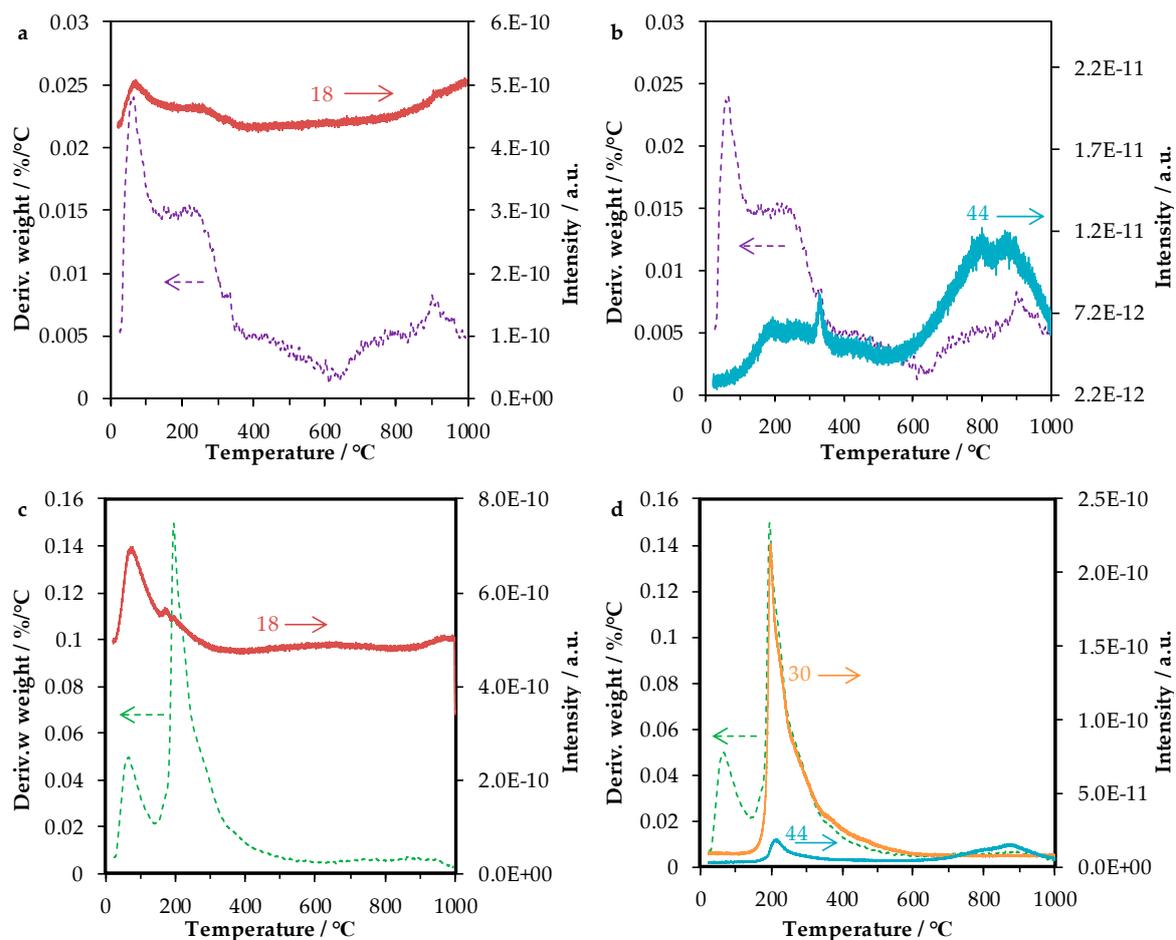


Figure S4. Evolution of $m/z = 18$, $m/z = 44$ and $m/z = 30$ as a function of temperature and Derived weight curve for the decomposition of (a-b) Hap and (c-d) Mn10Hap.

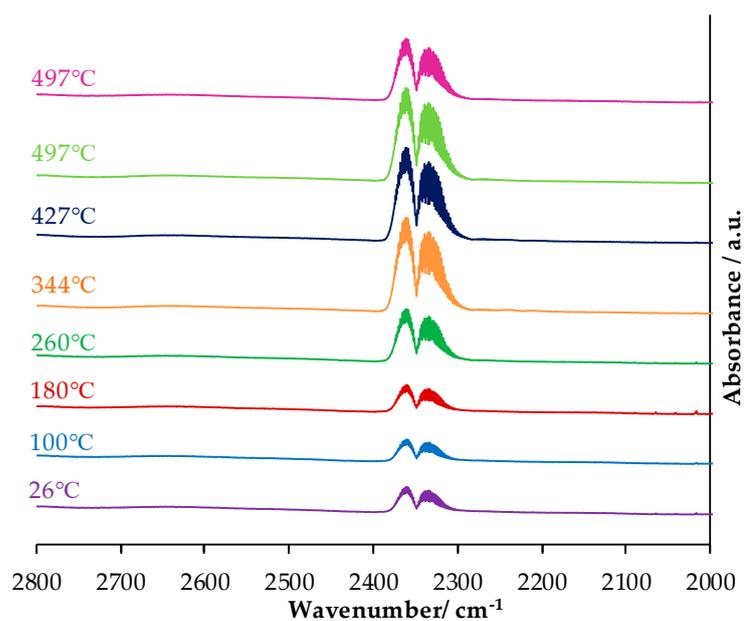


Figure S5. CO₂ production in the gas phase in the 2000-2800 cm⁻¹ window.