Supporting information

Effect of Thermal Treatment on Physicochemical Properties and Catalytic Activity of Minerals Acted as Catalysts in Heterogeneous Catalytic Ozonation

Savvina Psaltou [1], Efthimia Kaprara [2], Kyriaki Kalaitzidou [2], Manassis Mitrakas [2] and Anastasios Zouboulis [1,*]

[1] Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University; 54124 Thessaloniki, Greece; spsaltou@chem.auth.gr

[2] Laboratory of Analytical Chemistry, Department of Chemical Engineering, Aristotle University, 54214 Thessaloniki, Greece; kaprara@auth.gr (E.K.); kikalaitz@geo.auth.gr (K.K.); mmitraka@auth.gr (M.M.)

* Correspondence: zoubouli@chem.auth.gr

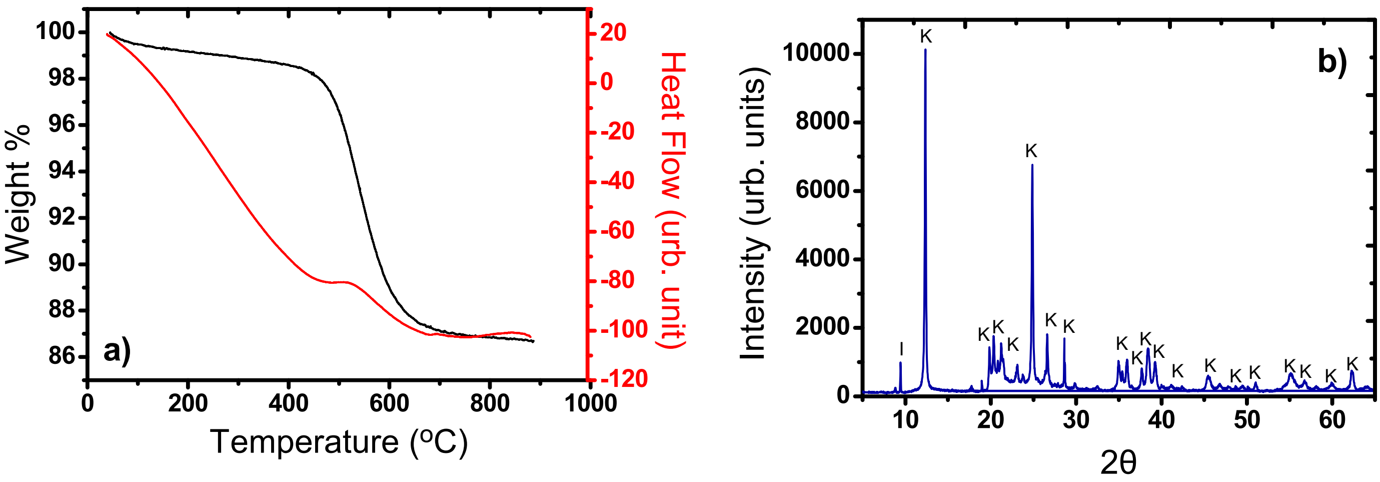

Figure S1. (a) TG/DTA and (b) XRD diagram of kaolin. Peaks for K: Kaolin, I: Illite.

Pages: 6, Figures: 5, Tables: 2, Text 1

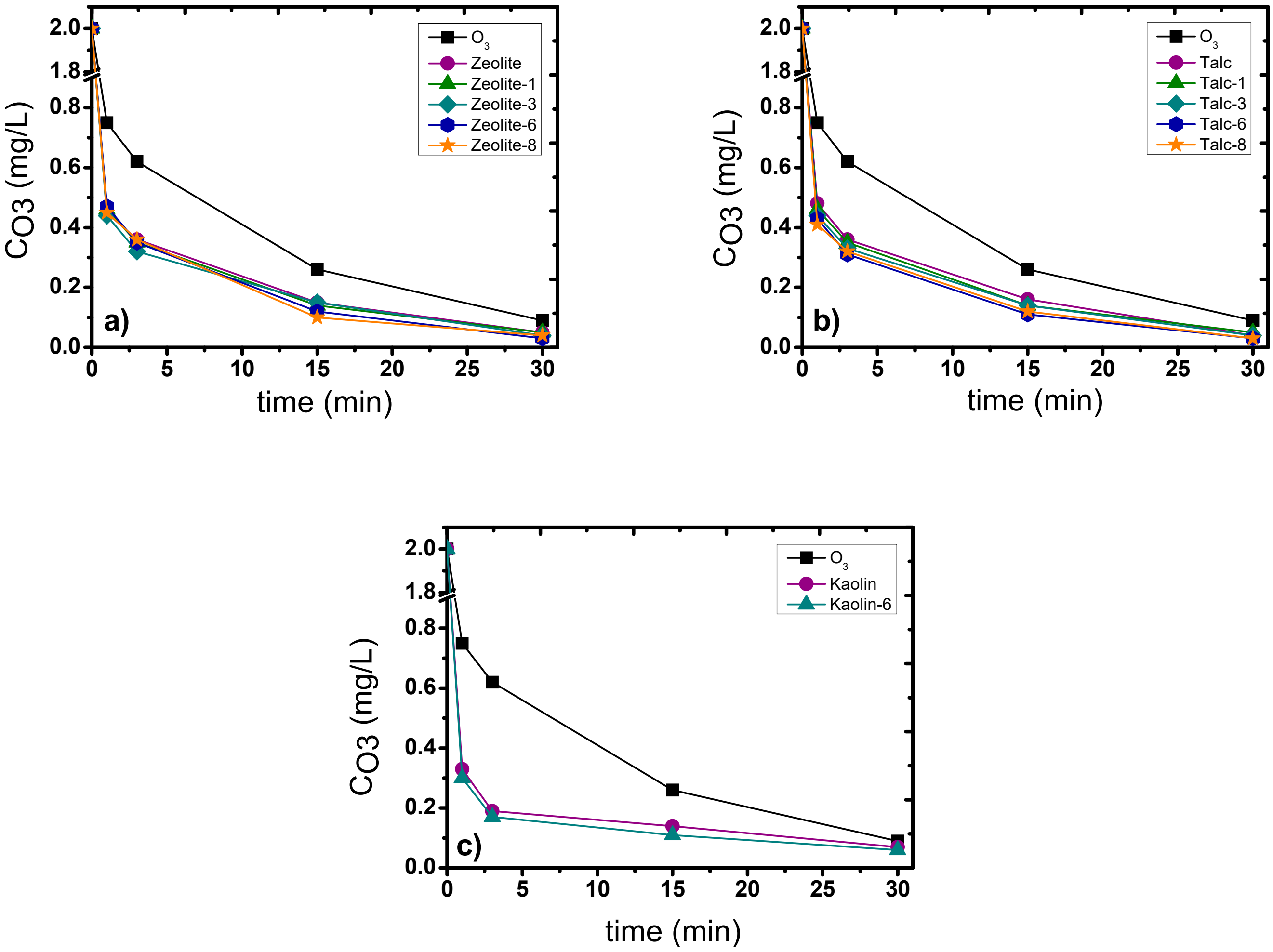

Figure S2. Influence of thermal pre-treatment on ozone decomposition in comparison to single ozonation: (a) zeolite, (b) talc, and (c) kaolin. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 μM, pH 7 and temperature 23 ± 2 °C.

Pages: 6, Figures: 5, Tables: 2, Text 1

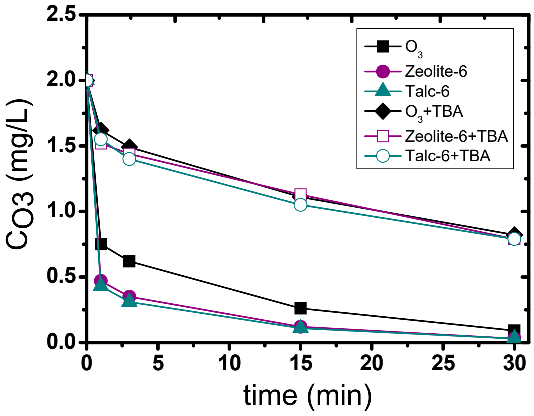

Figure S3. Effect of TBA addition on ozone decomposition in the catalytic ozonation systems, as compared to single ozonation. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, p-CBA concentration 4 μM, TBA concentration 0.4 mM, pH 7 and temperature 23 ± 2 °C.

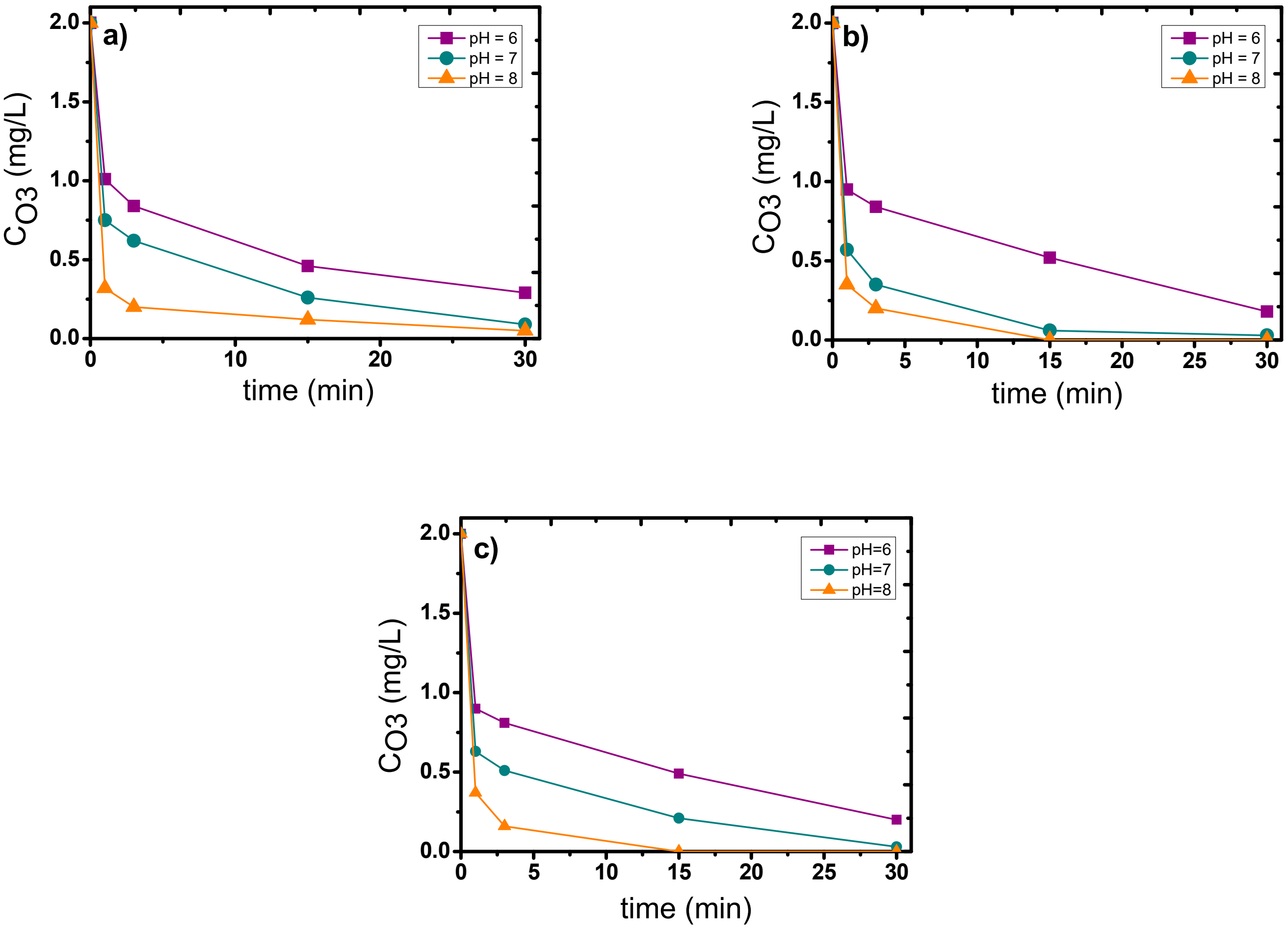

Figure S4. Effect of pH value on the decomposition of ozone; (a) Single ozonation, (b) zeolite-6, and (c) talc-6. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, initial p-CBA concentration 4 μM and temperature 23 ± 2°C.

Pages: 6, Figures: 5, Tables: 2, Text 1

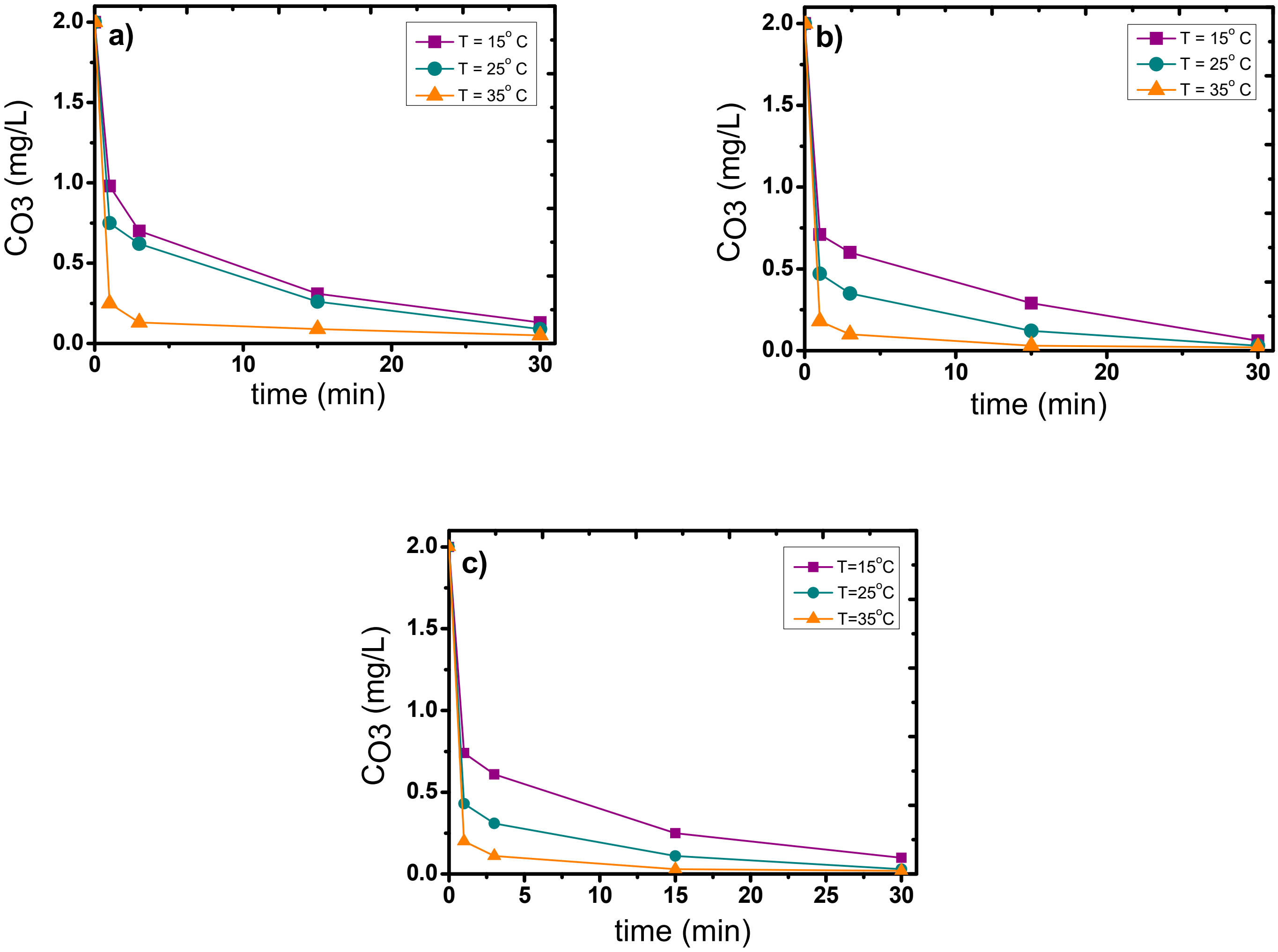

Figure S5. Effect of temperature on ozone decomposition; (a) Single ozonation, (b) zeolite-6, and (c) talc-6. Experimental conditions: ozone concentration 2 mg/L, catalyst concentration 0.5 g/L, initial p-CBA concentration 4 μM and pH 7.

Table S1. Adsorption capacity of examined natural minerals thermally pre-treated at various temperatures for the case of p-CBA removal. Experimental conditions: catalysts concentration 0.5 g/L, p-CBA concentration 4 μM, pH 7, temperature 23 ± 2 °C and adsorption time 30 min.

Catalyst	**q_t (μg p-CBA/ g catalyst)**
Zeolite	59.5
Zeolite-1	62.6
Zeolite-3	62.6
Zeolite-6	68.9
Zeolite-8	78.3
Talc	53.2
Talc-1	53.2
Talc-3	62.6
Talc-6	62.6
Talc-8	75.2
Kaolin	9.4
Kaolin-6	18.8

Pages: 6, Figures: 5, Tables: 2, Text 1

Table S2. Adsorption capacity of zeolite-6 and talc-6 for the case of p-CBA removal at various temperatures. Experimental conditions: catalysts concentration 0.5 g/L, p-CBA concentration 4 μM, pH 7 and adsorption time 30 min.

Temperature	**q_t (μg p-CBA/ g catalyst)**
	Zeolite-6
15 °C	216.1
25 °C	68.9
35 °C	50.10
	Talc-6
15 °C	134.7
25 °C	62.6
35 °C	53.2

Pages: 6, Figures: 5, Tables: 2, Text 1

Text S1. Example of calculation, regarding the theoretical escape of ozone from the water towards the gas/air phase during the oxidation experiment.

The following calculation was performed, aiming to simulate the real reaction/oxidationtreatment process, and in the example was conducted for the temperature 15 °C (288 K). The treatment jarcontained 250 mL of 2 mg/L O_3 and the headspace was 10 mL at the beginning of the reaction. Samples were taken at time intervals 0.1, 1, 3, 15 and 30 min and the amount of each sample was 5 mL. The calculations were conducted under the assumption that the equilibrium of ozone in the gas/aqueous interphase would be achieved immediately after each sample and that no ozone decomposition was occurred during the (fast) reaction.

Calculations:

The mole fraction of ozone (x_{ozone}) in a 2 mg/L ozone solution:

$$x_{ozone} = \frac{\frac{2\ mgL^{-1}}{48\ g\ mol^{-1}}}{\frac{1000\ gL^{-1}}{18\ g\ mol^{-1}}} = 7.5 * 10^{-7} \tag{1}$$

According to Henry's law and for $k_{288} = 1.27*10^5$ kPa, the partial pressure of ozone was:

$$p_{288} = k_{288} * x_{ozone} = 1.27 * 10^5 * 7.5 * 10^{-7} = 0.095\ kPa \tag{2}$$

The molar volume of the gas at 288 K was:

$$PV = nRT \leftrightarrow V = \frac{nRT}{P} = \frac{1\ mol * 0.082\ \frac{L\ atm}{mol\ K} * 288\ K}{1\ atm} = 23.6\ L \tag{3}$$

The headspace of the vessel was 10 mL and the molar volume of gas at 288 K was 23.6 L mol^{-1}, hence the amount of ozone in the headspace for the atmospheric pressure 101 kPa was:

$$\frac{10\ mL}{23.6\ L\ mol^{-1}} * \frac{0.095\ kPa}{101\ kPa} = 0.385\ \mu mol\ O_3 \tag{4}$$

The amount of ozone in water was:

$$\frac{2\ mgL^{-1} * 0.25\ mL}{48\ gmol^{-1}} = 10.41\ \mu mol\ O_3 \tag{5}$$

According to these calculations the escape amount of ozone in the gas phase at the beginning of the reaction was:

$$\left(\frac{0.385\ \mu mol\ O_3}{10.41\ \mu mol\ O_3}\right) * 100 = 3.7\% \tag{6}$$

Pages: 6, Figures: 5, Tables: 2, Text 1