Supplementary Materials to

Highly efficient mesoporous Mg/γ-Al_2O_3 catalysts for ozonation of saline petroleum effluents

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Abstract
γ-Al_2O_3 is promising for catalytic ozonation because it produces HO° radicals. To improve its basicity and/or its oxidative character, highly mesoporous γ-Al_2O_3 was doped with different metals M alone or in mixture (M = Mg, Ca, Zn, Fe, Ba, Zr, Cu, Co, Ni, Ce, Ti, with 0.05 < M/Al < 0.5 molar ratio) prepared either by incipient wetness deposition or by direct sol-gel. Tests to determine the basic and oxidative character of the catalysts have been set up. Results show that Mg-doped alumina materials exhibited the highest basicity and Cu,Mg-doped alumina materials the highest oxidative character. These materials (5 g/L) were tested in the catalytic ozonation of a synthetic saline (NaCl = 50 g/L) petroleum effluent such as produced water (TOC = 216 mg/L) containing phenols, acetic acid and polycyclic aromatic hydrocarbons. Among these catalysts, Mg-doped alumina (molar ratio Mg/Al = 0.1, 0.2) prepared by incipient wetness deposition were the more efficient catalysts. Under reuse the Mg-doped alumina catalyst (Mg/Al = 0.1) exhibited the highest ozonation rate with 98% TOC removal in 5 h. This remarkable behavior was attributed to the *in-situ* formation during ozonation of spinel ($MgAl_2O_4$) nanoparticles at the surface of Mg-doped alumina particles.

Table S1. Textural features of Mg/γ-Al_2O_3, Ca/γ-Al_2O_3 and Ba/γ-Al_2O_3 (with M/Al = 0.05) calcined at 600 °C.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
γ-Al_2O_3 (600°C)	10.2	0.55	234	134
Mg/γ-Al_2O_3	10.2	0.55	234	130
Ca/γ-Al_2O_3	9.6	0.63	205	190
Ba/γ-Al_2O_3	9.6	0.62	220	137

Table S2. Textural properties of M/Co/γ-Al_2O_3 with different molar ratios synthesized by impregnation, calcined at 600°C.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
0.1Fe/0.1Co/Al	9.8	0.43	152	511
0.5Co/Al	8.9	0.3	132	124
0.5Mg/0.5Co/Al	10.4	0.27	87	135
0.5Ca/0.5Co/Al	8.8	0.09	34	
0.5Cu/0.5Co/Al	10.6	0.2	74	164

Table S3. Textural properties of M/γ-Al_2O_3 calcined at 600 °C with M = Fe, Co, Ni, Cu, Zn, Ce with M/Al = 0.05.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
γ-Al_2O_3 (600°C)	10.2	0.55	234	134
Fe/γ-Al_2O_3	9.7	0.51	276	165
Co/γ-Al_2O_3	9.8	0.54	227	126
Ni/γ-Al_2O_3	9.8	0.59	250	140
Cu/γ-Al_2O_3	9.8	0.56	237	128
Zn/γ-Al_2O_3	9.8	0.53	233	110
Ce/γ-Al_2O_3	9.8	0.42	186	257
Zr/γ-Al_2O_3	10.0	0.8	293	116

Table S4. Textural properties of Cu/γ-Al_2O_3 samples with different Cu/Al molar ratios synthesized by impregnation, calcined at 600°C.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
Al_2O_3 (600°C)	10.2	0.55	234	134
Cu/Al=0.1	11.6	0.55	186	159
Cu/Al=0.2	11.5	0.55	195	102
Cu/Al=0.3	11.2	0.44	147	141
Cu/Al=0.4	9.8	0.41	140	136
Cu/Al=0.5	9.8	0.35	116	191

Table S5. Textural properties of Cu/γ-Al_2O_3 samples with different Cu/Al molar ratios synthesized by impregnation, calcined at 800°C.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
Cu/Al=0.1	21	0.53	117	118
Cu/Al=0.2	21.6	0.45	97	145
Cu/Al=0.3	25	0.26	26	/
Cu/Al=0.4	30	0.21	41	/
Cu/Al=0.5	25.2	0.23	46	88

Table S6. Textural properties of Cu/γ-Al_2O_3, Mg/γ-Al_2O_3 and Mg/Cu/γ-Al_2O_3 samples with different molar ratios synthesized by impregnation, calcined at 600°C.

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
Cu/Al=0.2	11.5	0.55	195	102
Mg/Al = 0.2	11.9	0.69	259	119
Mg/Cu/Al=0.2	11.4	0.41	153	126
Cu/Al=0.5	9.8	0.35	116	191
Mg/Cu/Al=0.5	10.3	0.26	97	108

Table S7. Results of BET surface area and porosity of γ-Al_2O_3 synthesized by sol-gel calcined at 600 and 800°C

Calcination temperature (°C)	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
600	7.28	0.84	441	112
800	8.0	0.65	233	123

Table S8. Results of BET surface area and porosity of γ-Al_2O_3 calcined at 800°C by sol-gel, and Ti-Al_2O_3 synthesized by sol-gel method and calcined at 750 °C

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
γ-Al_2O_3	8.0	0.65	233	123
Ti-Al_2O_3	4.83	0.27	238	101

Table S9. Results of BET surface area and porosity of γ-Al_2O_3 and 0.2 Cu-Al_2O_3 synthesized by sol-gel method and calcined at 600 °C

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
γ-Al_2O_3	7.3	0.84	441	112
Cu-Al_2O_3	4.8	0.26	214	101

Table S10. Results of BET surface area and porosity of Mg-Cu-Al_2O_3 synthesized by sol-gel method with different molar ratios and calcined at 600 °C

Materials	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
0.2 Mg/0.2 Cu/1 Al	6.5	0.44	297	115
0.5 Mg/0.5 Cu/1 Al	4 - 20	0.25	268	100

Table S11. Results of BET surface area and porosity of Ca-Cu-Al_2O_3 and Mg-Cu-Al_2O_3 (0.2:0.2:1) synthesized by sol-gel method, and calcined at 600 °C

Sample	$Ø_{pore}$ (nm)	V_{total} (ml/g)	S_{BET} (m^2/g)	C_{BET}
Ca-Cu-Al_2O_3	8.4	0.19	74	130
Mg-Cu-Al_2O_3	6.5	0.44	297	115

Table S12. Results of benzoic acid adsorption capacity of M/γ-Al_2O_3

Materials	Synthesis method	Metal / Al (molar ratios)	Calcination temperature	pH of solution	Benzoic acid adsorption (mmol/g)
γ-Al_2O_3		/	/	4.0	0.37
Mg/γ-Al_2O_3	impregnation	0.20	600	8.1	0
Mg/γ-Al_2O_3	impregnation	0.12	600	6.6	0
Mg/γ-Al_2O_3	impregnation	0.06	600	6.3	0
Mg/γ-Al_2O_3	impregnation	0.03	600	6.3	0.0037
Mg/γ-Al_2O_3	impregnation	0.015	600	5.0	0.24
Mg/γ-Al_2O_3	impregnation	0.03	450	6.2	0
Mg/γ-Al_2O_3	impregnation	0.03	750	4.3	0.25
Ca/γ-Al_2O_3	impregnation	0.07	600	7.0	0
Zn/γ-Al_2O_3	impregnation	0.05	600	4.3	0.24
Fe/γ-Al_2O_3	impregnation	0.05	600	3.8	0.0099
Ba/γ-Al_2O_3	impregnation	0.05	600	6.2	0
Zr/γ-Al_2O_3	impregnation	0.05	600	4.2	0.29
Cu/γ-Al_2O_3	impregnation	0.05	600	5.1	0.22
Co /γ-Al_2O_3	impregnation	0.05	600	4.7	0.23
Ni/γ-Al_2O_3	impregnation	0.05	600	4.2	0.26
Ce/γ-Al_2O_3	impregnation	0.05	600	4.4	0.27
Cu/γ-Al_2O_3	impregnation	0.1	600	5.2	0.24
Cu/γ-Al_2O_3	impregnation	0.2	600	5.2	0.24
Cu/γ-Al_2O_3	impregnation	0.3	600	5.3	0.22
Cu/γ-Al_2O_3	impregnation	0.4	600	5.4	0.21
Cu/γ-Al_2O_3	impregnation	0.5	600	5.4	0.16
Cu/γ-Al_2O_3	impregnation	0.1	800	5.5	0.14
Cu/γ-Al_2O_3	impregnation	0.2	800	5.4	0.10
Cu/γ-Al_2O_3	impregnation	0.3	800	5.4	0.10
Cu/γ-Al_2O_3	impregnation	0.4	800	5.3	0.08
Cu/Mg/γ- Al_2O_3	impregnation	0.1:0.1:1	600	5.9	0.05
Cu/Mg/γ- Al_2O_3	impregnation	0.2:0.2:1	600	6.8	0
Co/γ-Al_2O_3	impregnation	0.5	600	4.8	0.25
Mg/Co/γ-Al_2O_3	impregnation	0.5	600	6.7	0.07
Ca/Co/γ-Al_2O_3	impregnation	0. 5	600	6.7	0.03
Cu/Co/γ-Al_2O_3	impregnation	0. 5	600	5.7	0.16
Mg/Cu/γ-Al_2O_3	impregnation	0.2	800	5.8	0.09
Al_2O_3	sol-gel	0	750	5.0	0.33
Ti-Al_2O_3	sol-gel	0.25	750	4.7	0.18
Cu-Mg-Al_2O_3	sol-gel	0.2:0.2:1	600	7.9	0.06
Cu-Mg-Al_2O_3	sol-gel	0.2:0.2:1	800	5.1	0.05
Cu-Mg-Al_2O_3	sol-gel	0.5:0.5:1	600		
Cu-Al_2O_3	sol-gel	0.2	600	5.2	0.19
Cu-Al_2O_3	sol-gel	0.2	800	5.2	0.17
Cu-Ca-Al_2O_3	sol-gel	0.2:0.2:1	600	6.3	0.06
Cu-Ca-Al_2O_3	sol-gel	0.2:0.2:1	800	5.7	0.07
Ce-Al_2O_3	sol-gel	0.1	600	5.2	0.34

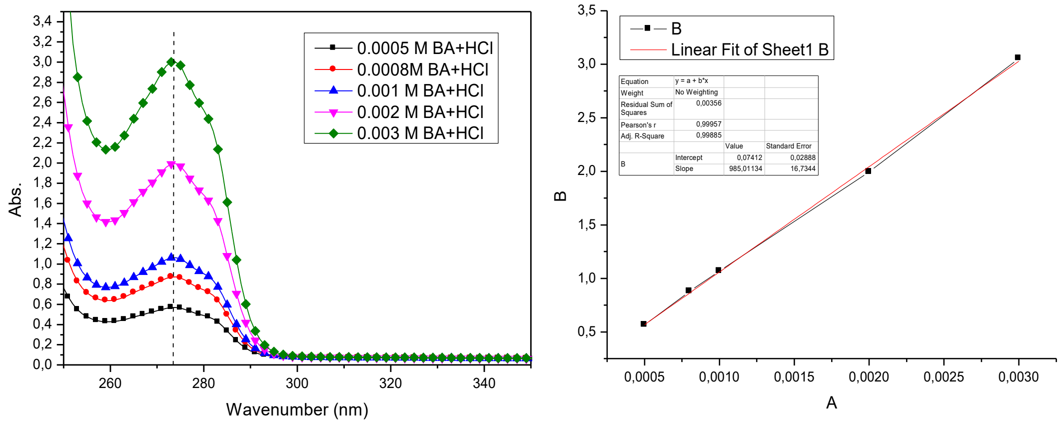


Fig S1. (left) UV spectra of benzoic acid at different concentrations. (right) Calibration curve of benzoic acid concentration with UV absorbance at 273 nm with pH adjustement below pH 2.

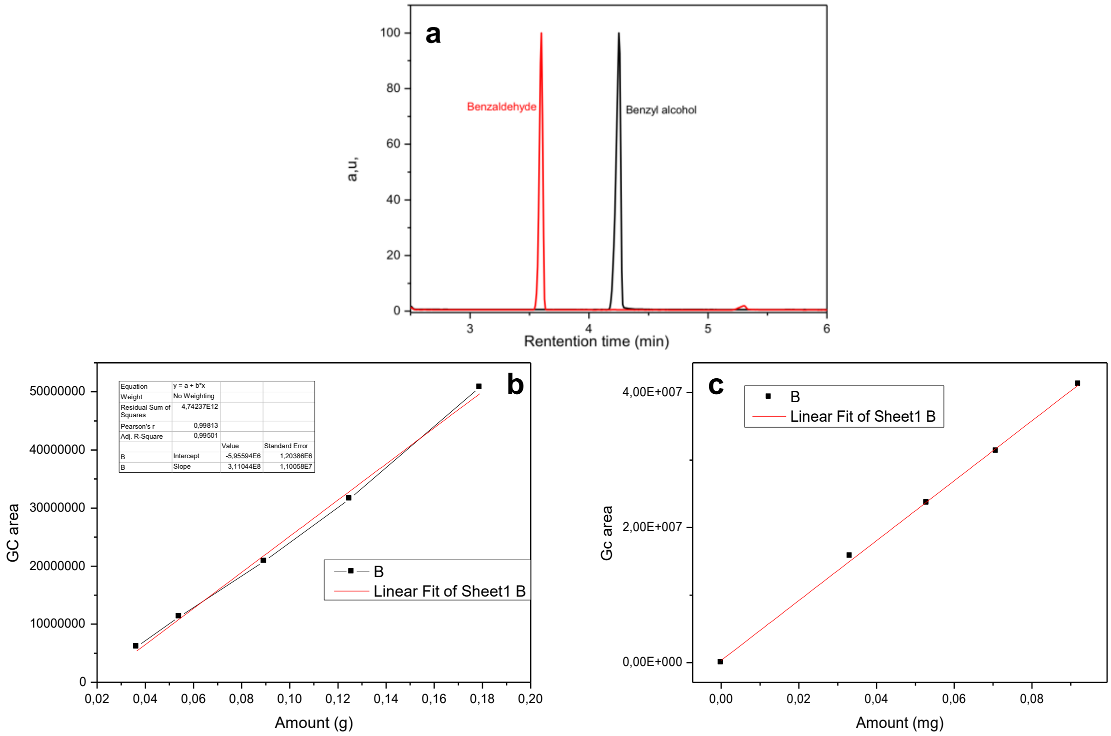


Fig S2. (a) GC specta of benzyl alcohol and benzaldehyde. Calibration curves of (b) benzyl alcohol and (c) benzaldehyde from GC spectra.

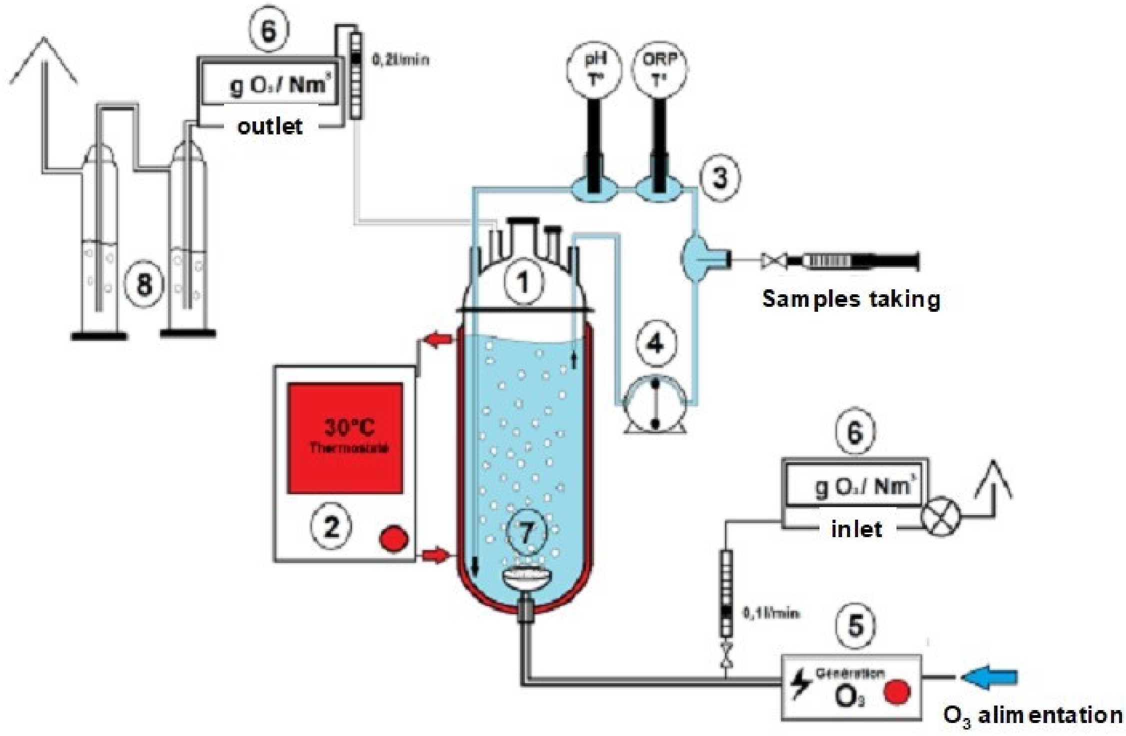


Fig S3. Schematic representation of ozonation reactor unit.

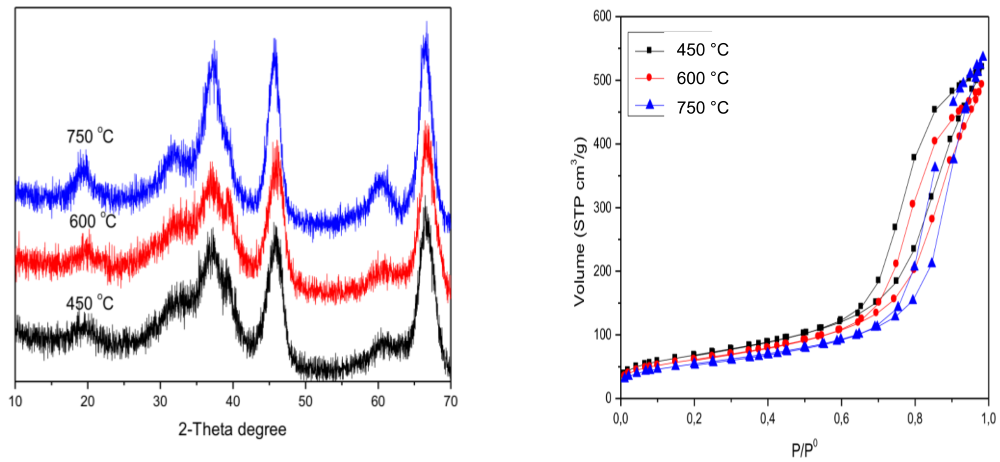


Fig. S4. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of Mg/γ-Al_2O_3 (Mg/Al = 0.05) calcined at different temperature from 450 to 750°C.

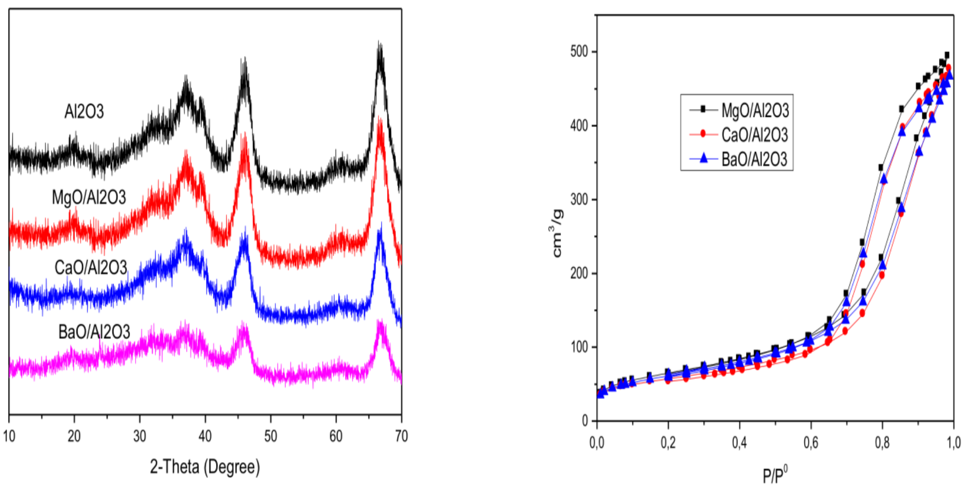


Fig. S5. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of γ-Al_2O_3, Mg/γ-Al_2O_3, Ca/γ-Al_2O_3 and Ba/γ-Al_2O_3 with M/Al = 0.05 calcined at 600 °C.

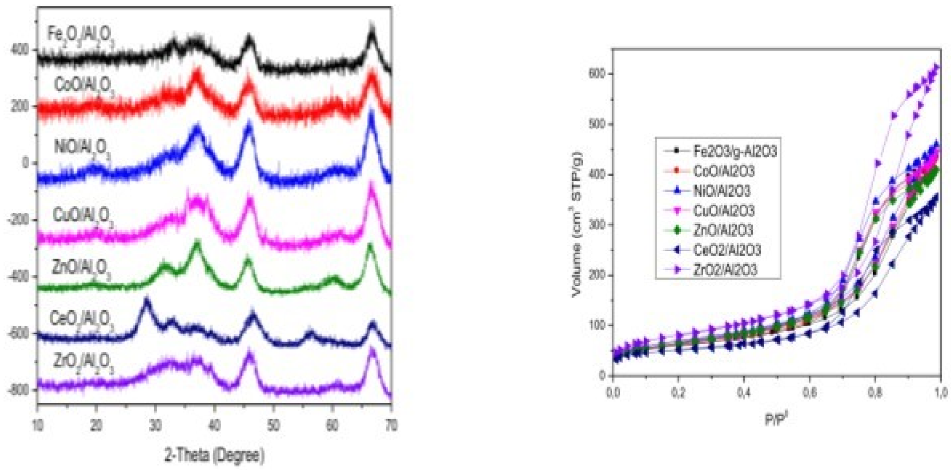


Fig. S6. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of M/γ-Al_2O_3 with M/Al = 0.05 calcined at 600 °C for M = Fe, Co, Ni, Cu, Zn, Ce, Zr.

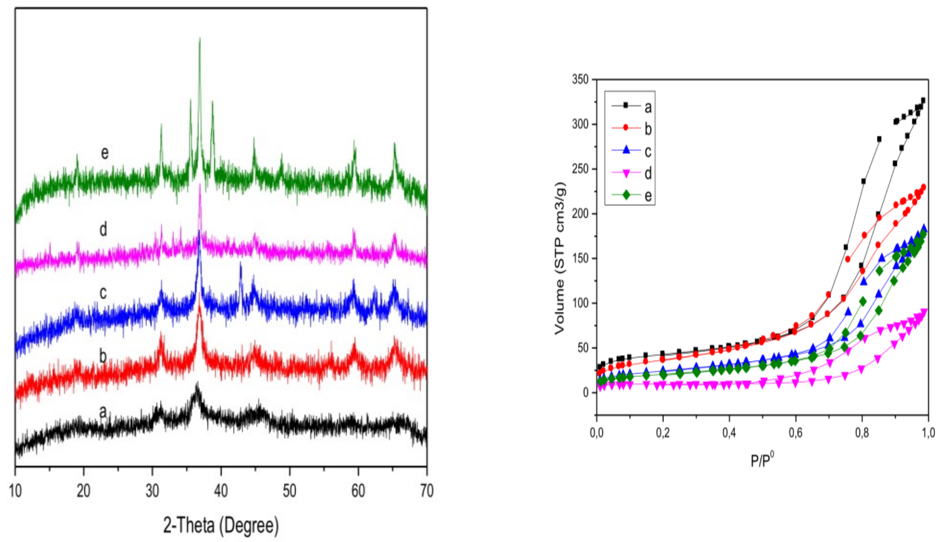
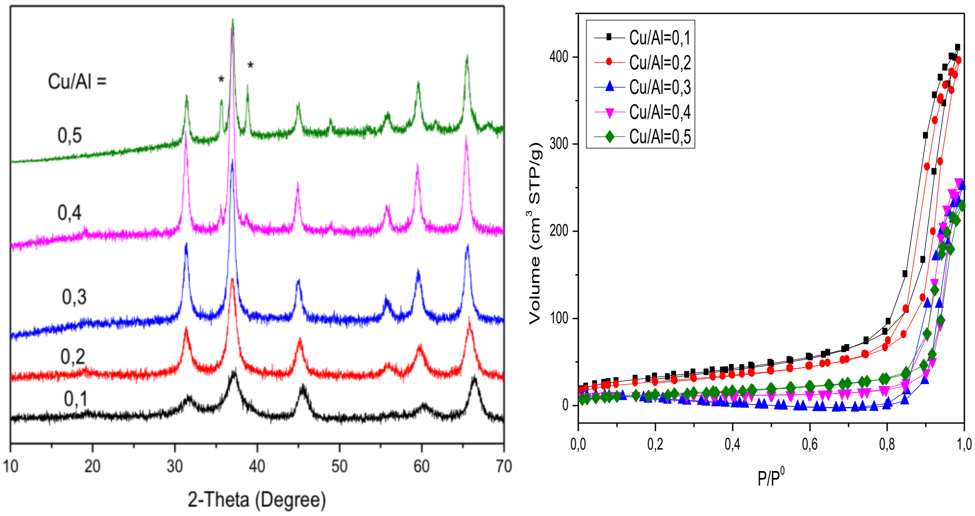


Fig. S7. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K M/Co/γ-Al_2O_3 samples and calcined at 600 °C: (a) Fe/Co/γ-Al_2O_3 (Fe/Co/Al = 0.1/0.1/1), (b) Co/γ-Al_2O_3 (Co/Al = 0.5/1), (c) Mg/Co/γ-Al_2O_3 (Mg/Co/Al=0.5/0.5/1), (d) Ca/Co/γ-Al_2O_3 (Ca/Co/Al = 0.5/0.5/1), (e) Cu/Co/γ-Al_2O_3 (Cu/Co/Al = 0.5/0.5/1).



* phase

Fig. S8. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of Cu/γ-Al_2O_3 materials prepared with different Cu/Al molar ratios and calcined at 800 °C. For Cu/Al = 0.1, 0.2, 0.3 structure of cubic spinel phase $CuAl_2O_4$ peaks: (220), (311), (400) and for Cu/Al = 0.4, 0.5 additional CuO NPs (*).

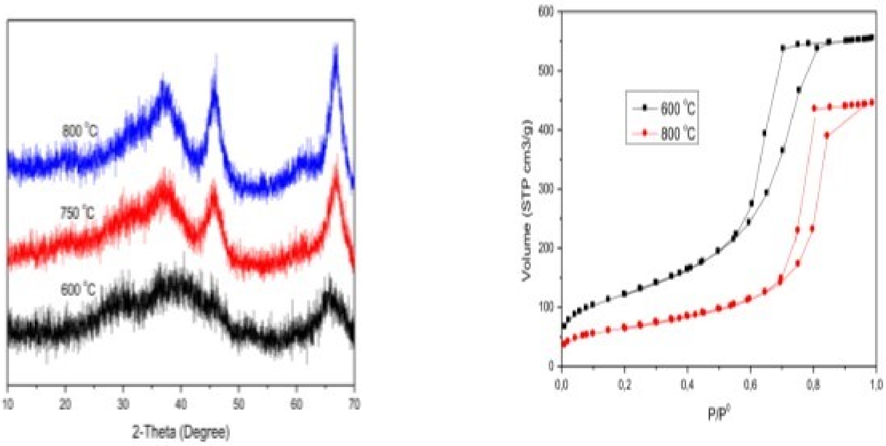


Fig. S9. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of Al_2O_3 synthesized by sol-gel method and calcined at 600, 750 and 800 °C.

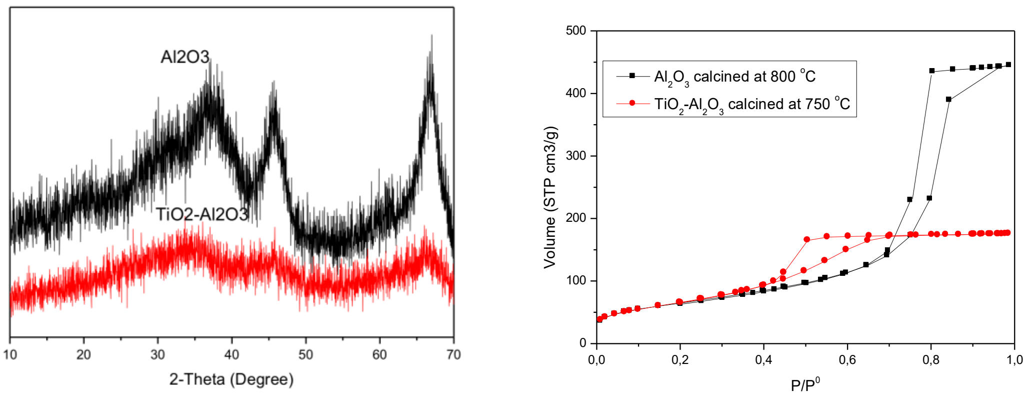


Fig. S10. (left) XRD patterns and (right) nitrogen sorption isotherms at 77 K of Al_2O_3 and Ti/Al_2O_3 synthesized by sol-gel method and calcined at 750 °C.

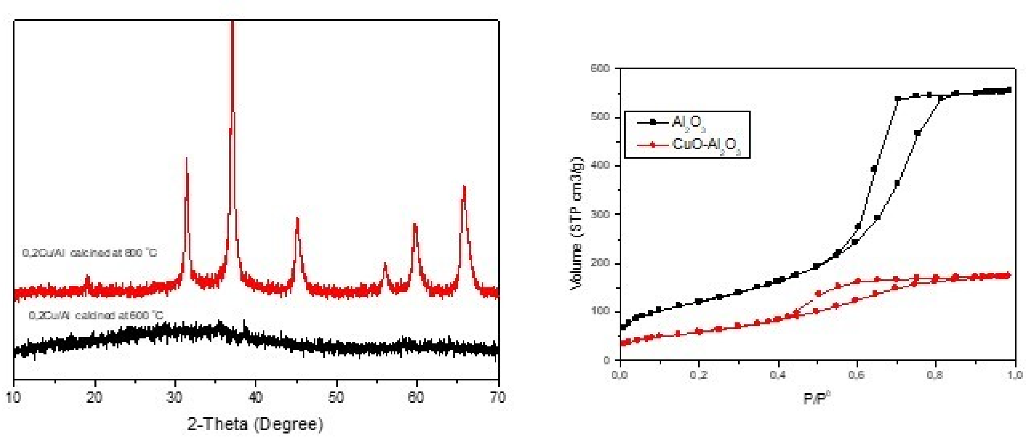


Fig. S11. (left) XRD patterns of Cu/Al_2O_3 synthesized by sol-gel method (sg) with Cu/Al = 0.2 and calcined at 600 °C and 800 °C revealing the cubic spinel structure and (right) nitrogen sorption isotherms at 77 K of Cu/Al_2O_3 (sg) and Al_2O_3 (sg) calcined at 600 °C.

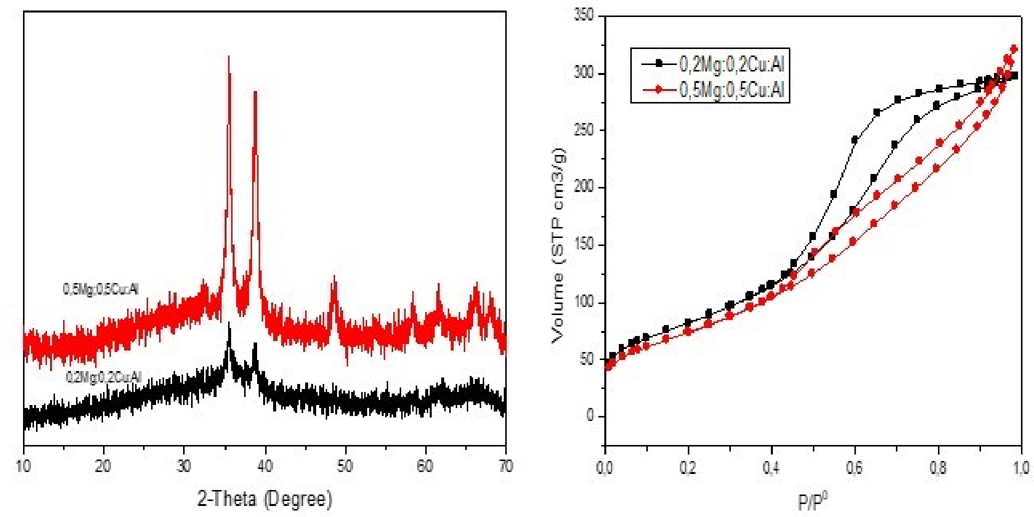


Fig. S12. (left) XRD pattern and (right) nitrogen sorption isotherms at 77 K of $Mg/Cu/Al_2O_3$ synthesized by sol-gel method with different molar ratios Mg/Cu/Al = 0.2/0.2/1 (black) and 0.5/0.5/1 (red), and calcined at 600 °C.

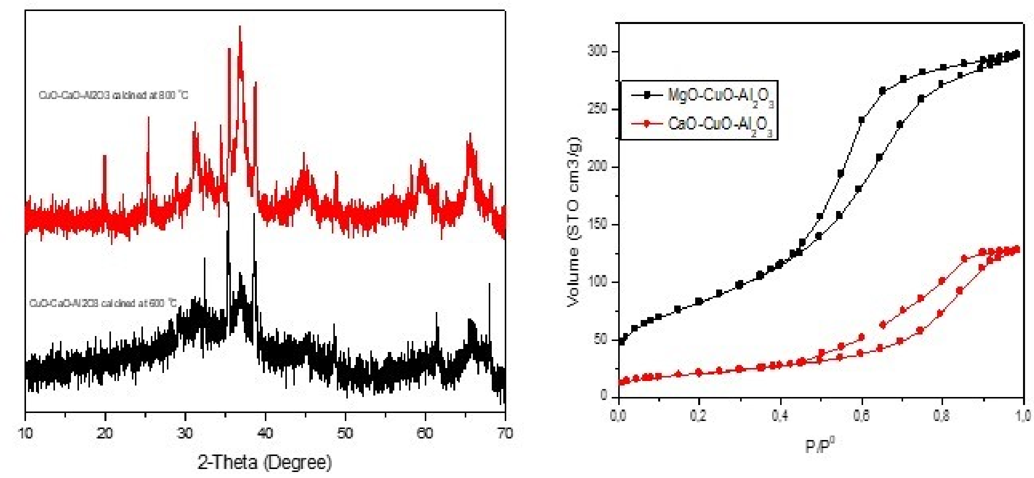


Fig. S13. (left) XRD pattern and (right) nitrogen sorption isotherms at 77 K of $Ca/Cu/Al_2O_3$ (Ca/Cu/Al = 0.2/0.2/1) synthesized by sol-gel method, and calcined at 600 and 800°C.

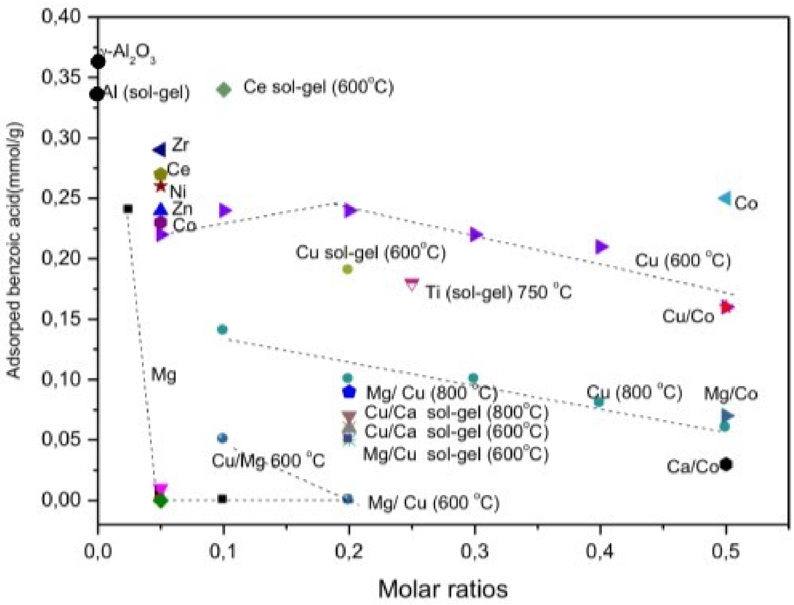


Fig. S14. Amount of benzoic acid adsorbed in the different materials (M/γ-Al_2O_3) prepared by incipient wetness impregnation or sol-gel method after 4 h of contact with the benzoic acid solution.

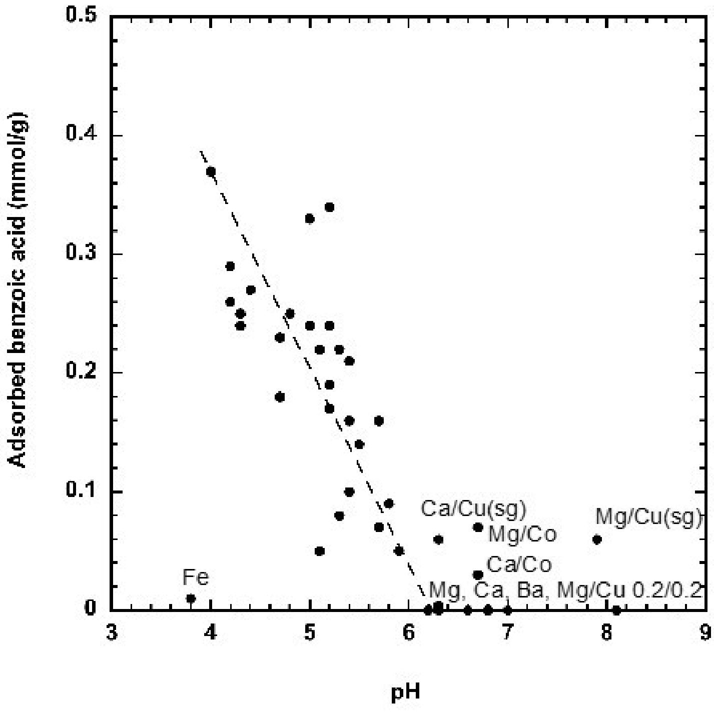


Fig. S15. Amount of benzoic acid adsorbed as a function of pH of the solution.

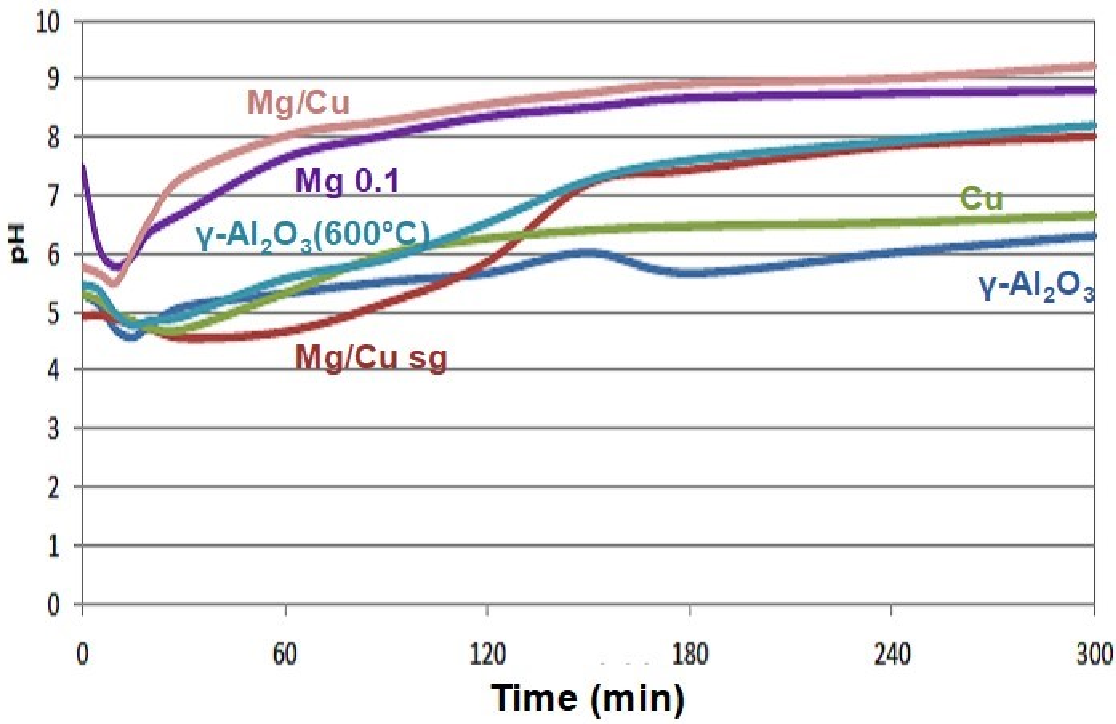


Fig. S16. pH of the saline petroleum effluent (initial pH = 3 - 4) as a function of ozonation time for the catalysts (5 g/L): uncalcined γ-Al_2O_3, calcined γ-Al_2O_3 (600 °C) and mixed-oxides calcined at 600 °C Mg/Cu/γ-Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1), Mg/γ-Al_2O_3 (Mg/Al = 0.1), Cu/γ-Al_2O_3 (Cu/Al = 0.2), Mg/Cu/Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1) prepared by sol-gel (sg).

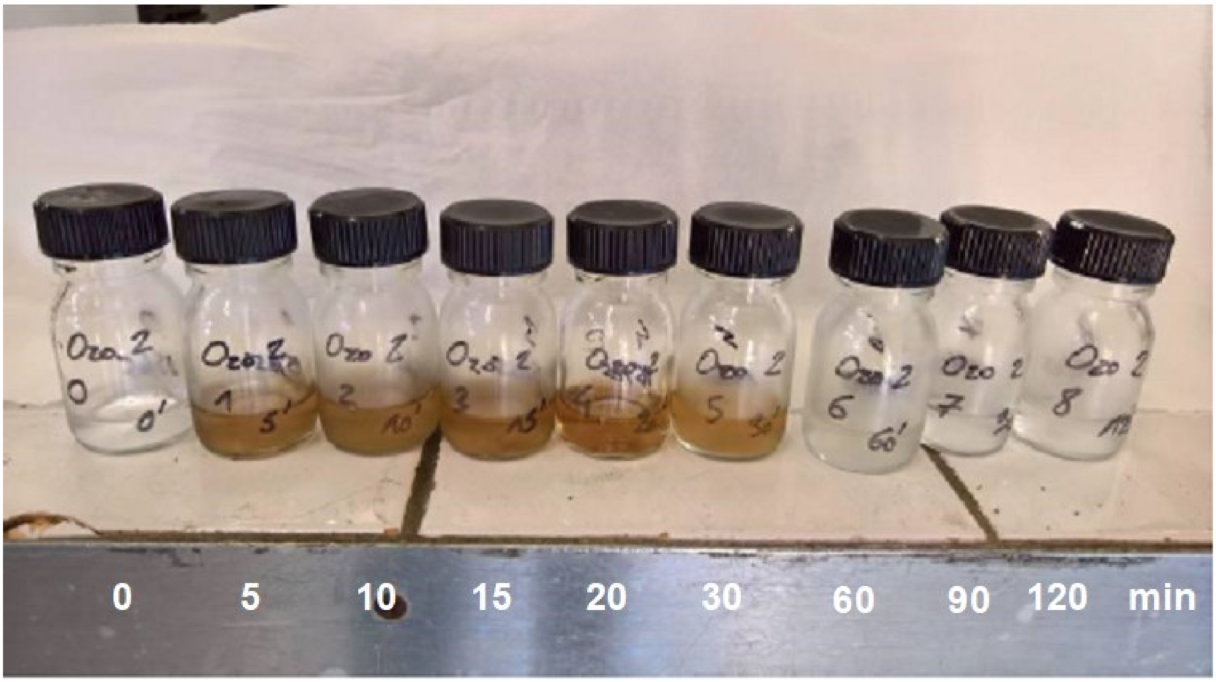


Fig. S17. Evolution of the colour of the effluent during catalytic ozonation. Example given for Cu/γ-Al_2O_3 (Cu/Al = 0.2) as catalyst.

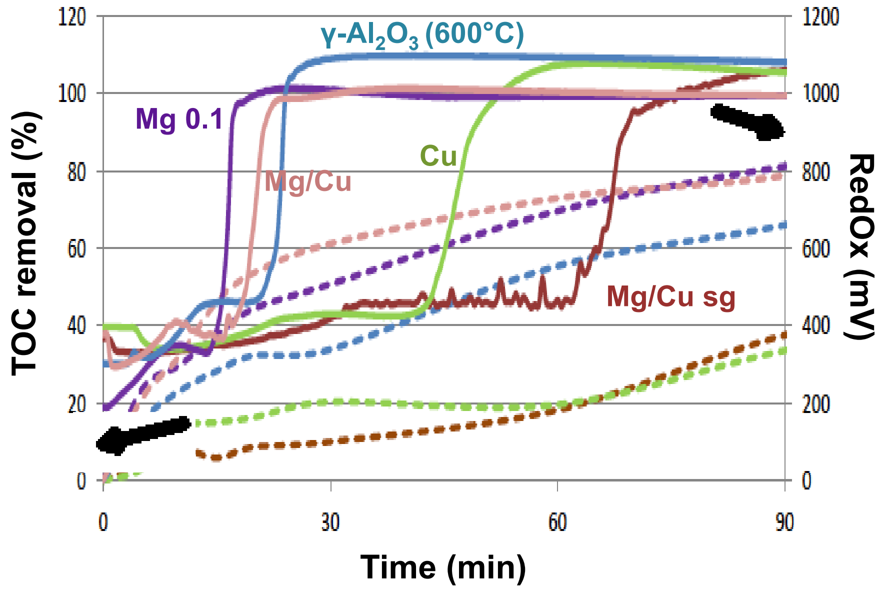


Fig. S18. (plain line) RedOx potential (initial 350 mV) and (dashed line) TOC removal of the saline petroleum effluent as a function of ozonation time for the catalysts (5 g/L): calcined γ-Al_2O_3 (600 °C) and mixed-oxides calcined at 600 °C Mg/Cu/γ-Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1), Mg/γ-Al_2O_3 (Mg/Al = 0.1), Cu/γ-Al_2O_3 (Cu/Al = 0.2), Mg/Cu/Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1) prepared by sol-gel (sg).

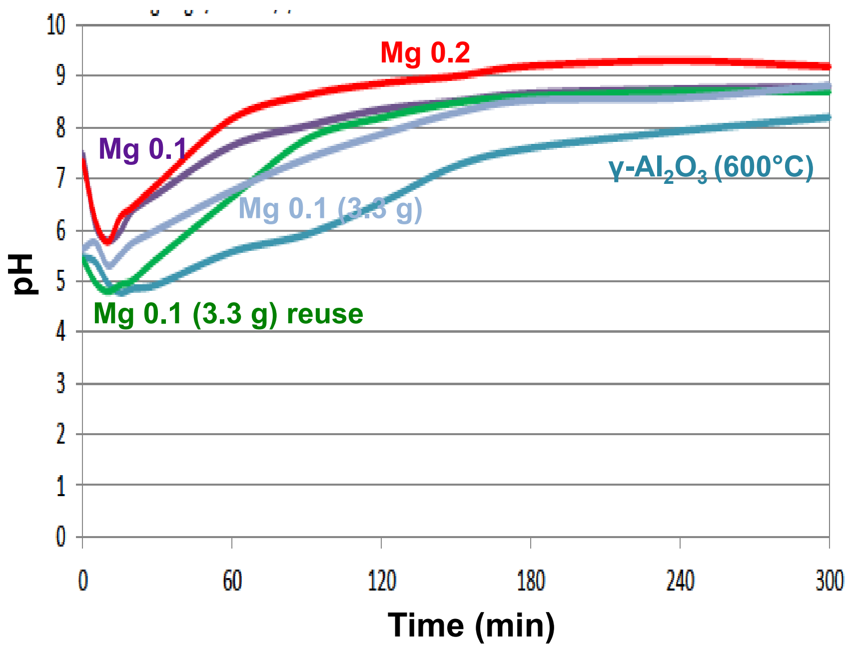


Fig. S19. pH of the saline petroleum effluents (initial pH = 3 - 4) as a function of ozonation time for different catalysts calcined at 600 °C with different amount of catalysts: γ-Al_2O_3 (600 °C) (5 g/L) and mixed-oxides Mg/γ-Al_2O_3 (Mg/Al = 0.1) (3.3 and 5 g/L) and in reuse (3.3 g/L), Mg/γ-Al_2O_3 (Mg/Al = 0.2) (5 g/L).

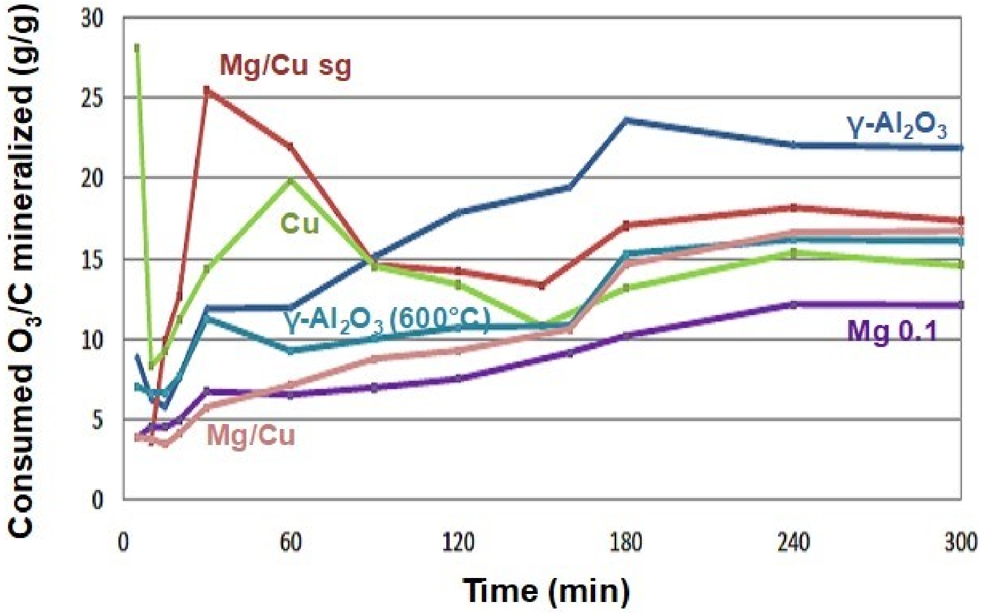


Fig. S20. Consumed ozone per g of mineralized Carbon as a function of ozonation time for the catalysts (5 g/L): uncalcined γ-Al_2O_3, calcined γ-Al_2O_3 (600 °C) and mixed-oxides calcined at 600 °C Mg/Cu/γ-Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1), Mg/γ-Al_2O_3 (Mg/Al = 0.1), Cu/γ-Al_2O_3 (Cu/Al = 0.2), Mg/Cu/Al_2O_3 (Mg/Cu/Al = 0.2/0.2/1) prepared by sol-gel (sg).

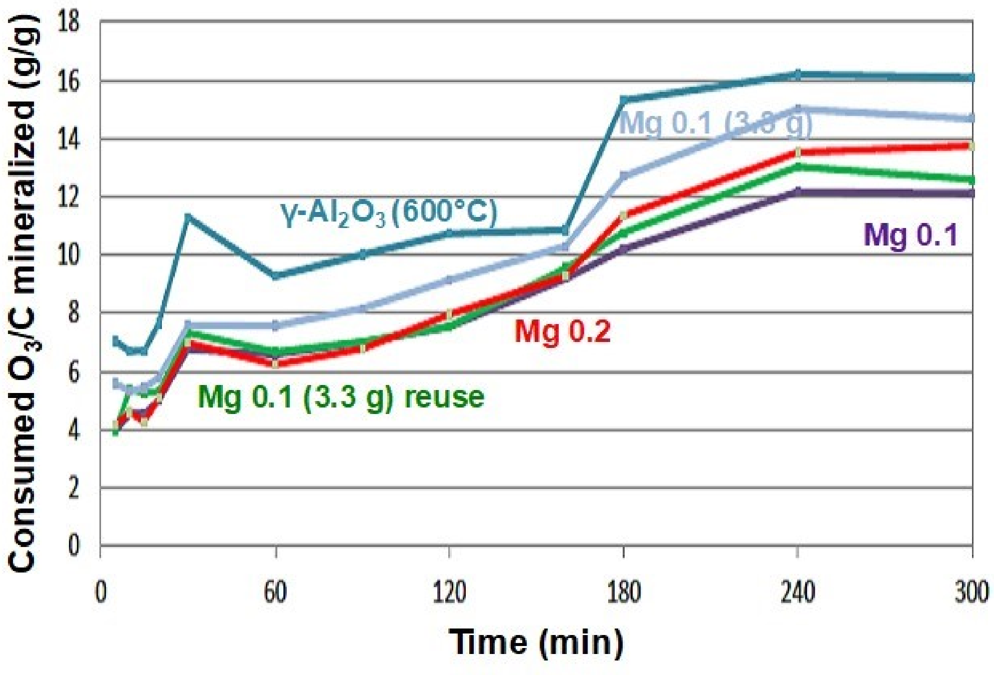


Fig. S21. Consumed ozone per g of mineralized Carbon as a function of ozonation time for different catalysts calcined at 600 °C with different amount of catalysts: γ-Al_2O_3 (600 °C) (5 g/L) and mixed-oxides Mg/γ-Al_2O_3 (Mg/Al = 0.1) (3.3 and 5 g/L), Mg/γ-Al_2O_3 (Mg/Al = 0.2) (5 g/L), and reuse of Mg/γ-Al_2O_3 (Mg/Al = 0.1) (3.3 g/L).

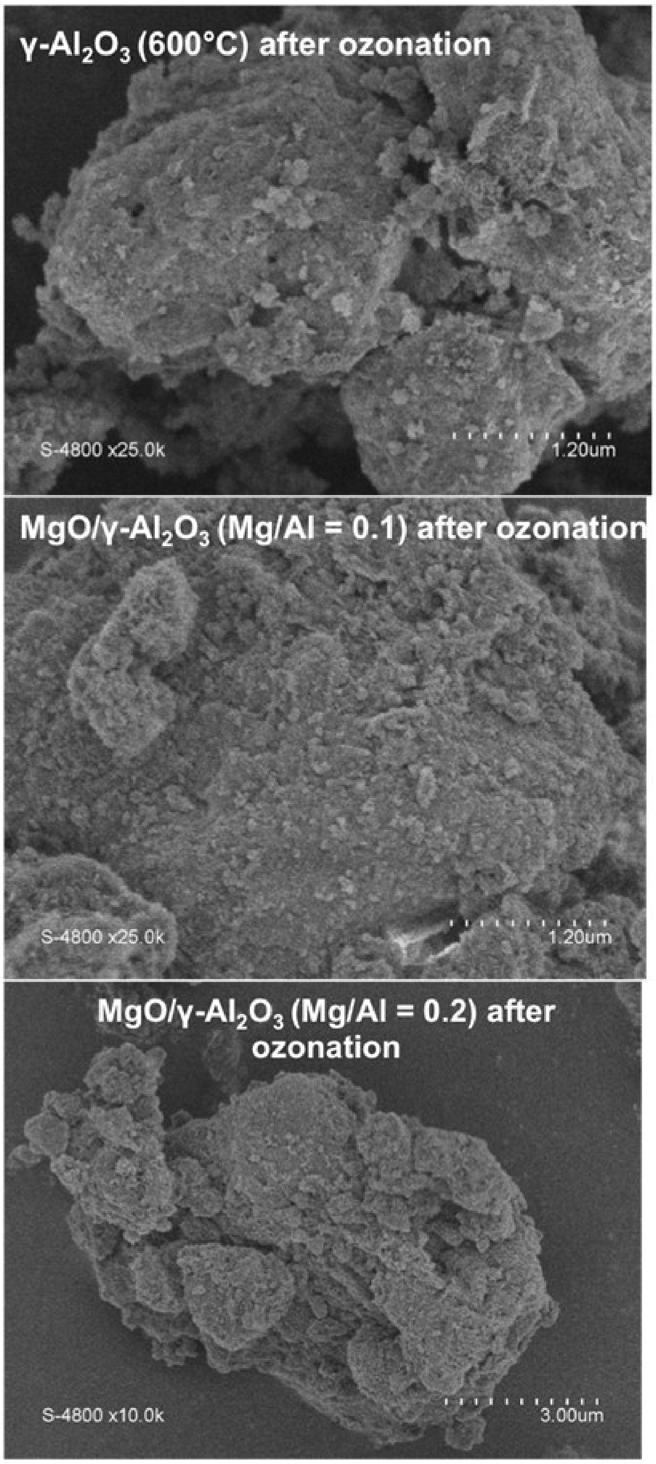


Fig. S22. SEM pictures of catalysts after ozonation: γ-Al_2O_3 (600 °C) and mixed-oxides Mg/γ-Al_2O_3 (Mg/Al = 0.1 and 0.2).

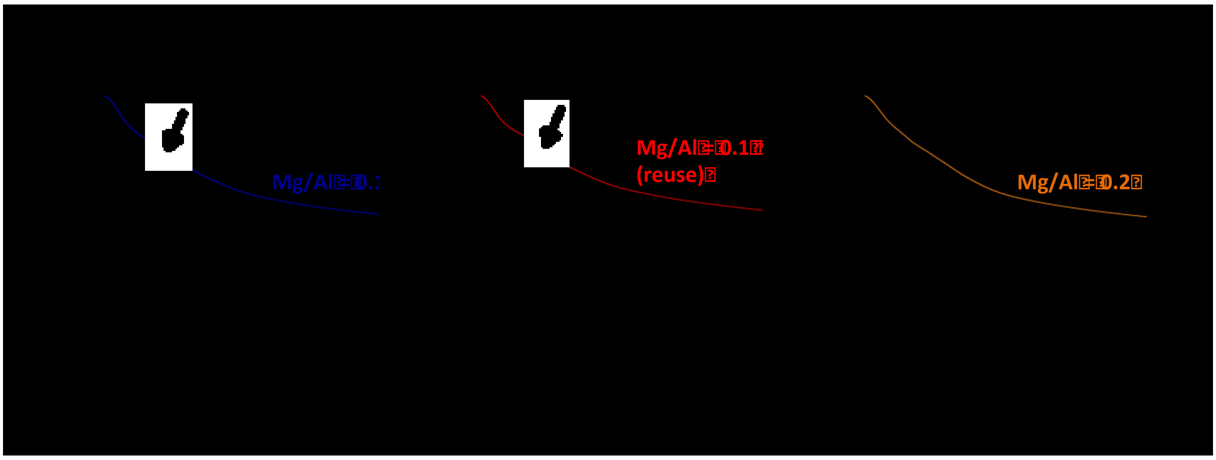


Fig. S23. TGA of catalysts after ozonation: γ-Al_2O_3 (600 °C), mixed-oxides Mg/γ-Al_2O_3 (Mg/Al = 0.1 and 0.2) and Mg/γ-Al_2O_3 (Mg/Al = 0.1) (reuse) after the second ozonation. (arrow) weight loss due presumably to trapped water into orthorhombic spinel $MgAl_2O_4$ structure.