Electronic Supplementary Material (ESI) for RSC Advances.

SUPPLEMENTARY INFORMATION

1. Characterization of NiO

Fig. S1 shows the SEM images of NiO used for the experiments. The images were obtained with a JEOL JSM 6701F at 20000x and 100000x. In **Fig. S1** b), the formation of clusters with an inferior length to 100 nm is recognized (These data coincide with the provider specifications). **Fig. S2a)** shows the NiO diffractogram obtained in a Bruker D8 advance with radiation operating at 35 kV and 25 mA (CuKα, λ= 1.54Å) in 2θ between 20-90°. The phase identification with MATCH3!® confirmed the trigonal structure with hexagonal axes of NiO. The information card of the 96-152-6381 entry was used for comparison purposes. The estimated density of NiO was 6.83 g cm^{-3}. The XRD patterns agree with the reported by Tiwari S & Rajeev K , and Yue W & Zhou W. They report the NiO DRX patterns of the Millers index of (111), (200), (220), (311) and (222). **Fig. S2b)** shows the XPS spectra of NiO with the characteristic patterns for C, Ni, and O. The results coincide with the reported by Yun-Guang et al, and Soleimampour et al. for NiO.

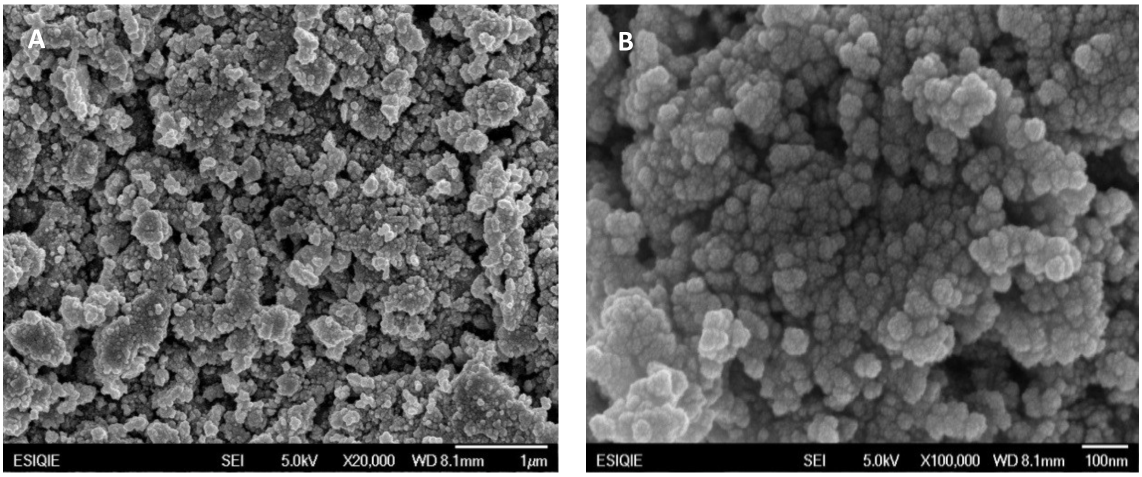


Fig. S1 SEM images of NiO without ozonation A) 20000x, B) 100000x.

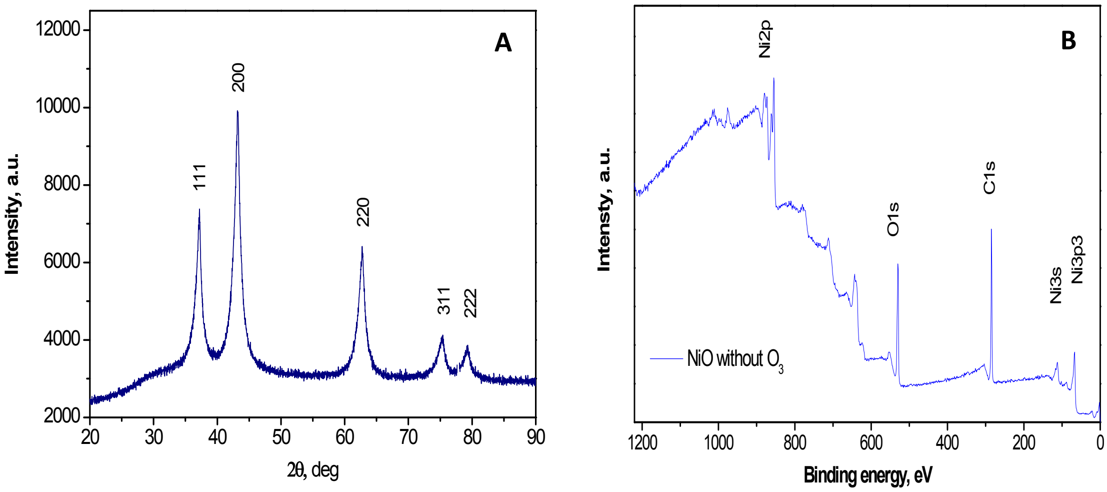


Fig. S2 A) XRD patterns and B) XPS of NiO without ozonation.

2. Identification of byproducts during naproxen ozonation

Byproducts identification was realized in two steps. In the first step, High-Performance Liquid Chromatography (HPLC) was used as analytic technique. The collected samples from the ozonation treatments were filtered into a 0.2 µm syringe filter before injection. The samples injection was carried out in a C18 column. Oxalic acid and naproxen were identified by HPLC using the method of external standard. The oxalic acid is a short chain organic acid which is the main byproduct of conventional ozonation treatments. The chromatographic technique also allows the identification of a signal of byproduct at a 12.9 min retention time which is attributed to a derived byproduct of the naproxen ozonation.

In the second step, the selected analytical technique was Electrospray Ionization coupled to Mass Spectrometry (ESI-MS). The technique used in negative mode generates a weak ionization in the components of the injected sample. Under such ionization condition, the obtained signals relate to molecular weights of byproducts in the sample. The treated samples were also filtered with a 0.2 µm syringe filter before injection. The ESI-MS study was exerted for the samples collected at the 5- and 60-min of ozonation treatments. **Fig.S3 a)** shows the ion associated with naproxen (M-H) 229.09 m/z with a molecular weight of 230.29 from the ESI-MS analysis. In contrast, **Fig. S3 b) and c)** show the ions related to the byproducts of the conventional and catalytic ozonation treatments of naproxen after 60 min of treatment. The identified ions were 149.06, 177.05, 205.09, 217.09, 249.08 m/z. The m/z ions (detected in the tandem analysis of ESI-MS) were evaluated by the ESI-MS-MS technique with the same analysis conditions fixing the appropriate mass. This technique produces patterns of ions distributions by the Bruker Compass Data Analysis 4.0 (Bruker Daltonics). The analysis of each ion fragment (with ChenBioDraw chemical structure database) yields the byproducts chemical structure (**Fig. S4**). The proposed chemicals structures allows suggesting a reaction pathway (Fig. 4 in the manuscript).

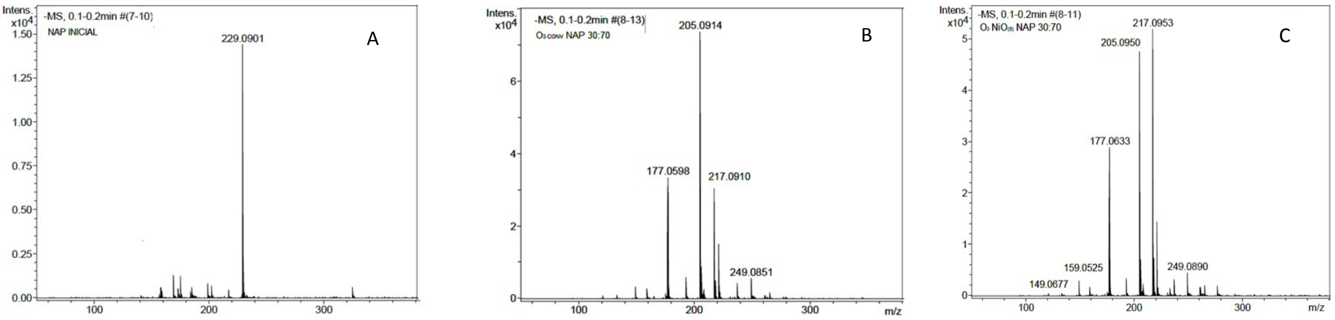
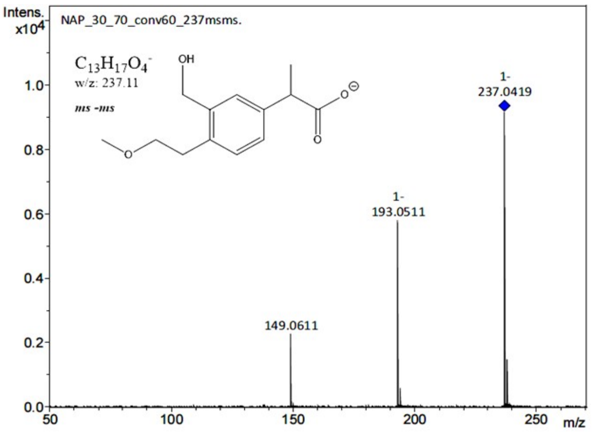
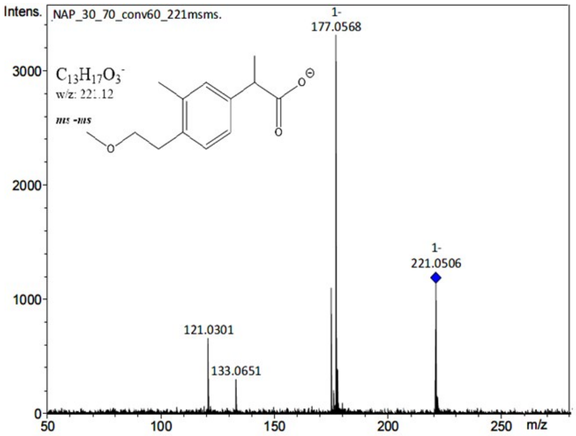
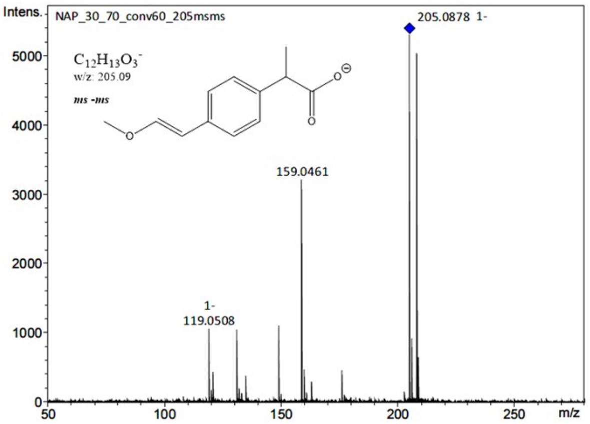


Fig. S3 ESI-MS spectra of the conventional and catalytic ozonation treatments of naproxen. A) Fresh sample, B) O_3 –conv 30:70. C) O_3 $NiO_{(s)}$ 30:70 at 60 min of reaction.







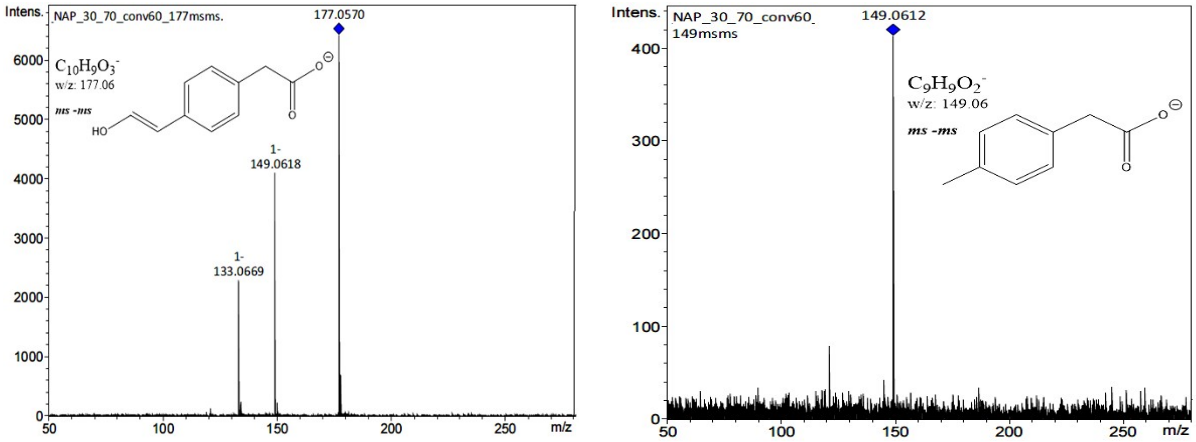


Fig. S4. ESI-MS-MS of m/z signals detected in the degradation of naproxen by ozone and the proposed byproducts.

3. Effect of ethanol on intermediates removal

Ethanol inhibits the degradation of both naproxen and byproducts along the ozonation. This fact can be demonstrated with the results of the ESI-MS and the non-identified intermediate with retention time at 12.9 min (HPLC), **Fig. S5**. The ESI-MS spectra (**Fig S5 a-c)** show the results of the treatments (from the samples collected at 60-min of catalytic ozonation) with several ratios of ethanol:water. Notice that the higher ethanol concentration, the slower degradation of non-identified intermediate. In the case without ethanol, **Fig. S5a** shows no characteristic signal in the ESI-MS study of samples corresponding to 60 min. However, for 5 min samples, there are similar ions m/z patterns to the ones observed with 60 min samples and 30 and 50 % of ethanol (**Fig S6**). This similarity indicates that ethanol presence retarded the byproducts formation or elimination during naproxen ozonation. The calculated degradation rate constants of non-identified byproduct (HPLC) confirmed the ethanol effect (**Table 2, in the manuscript**).

Ethanol %v		
0%	30%	50%

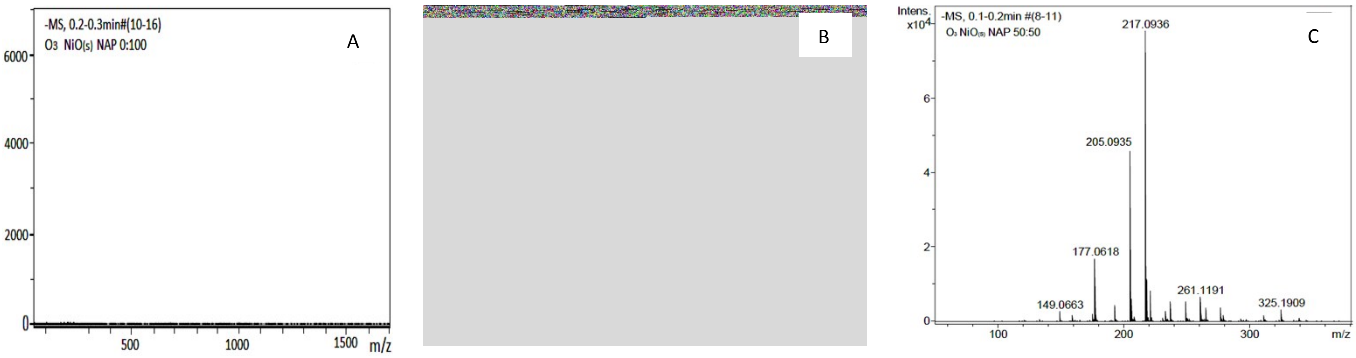


Fig. S5 – ESI-MS analysis of NAP ozonation in presence of NiO at 60 min in several ratio of ethanol:water a) 0:100, b) 30:70 and c) 50:50.

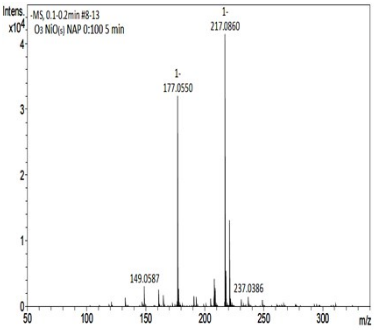


Fig. S6 ESI-MS analysis of NAP ozonation in presence of NiO at 5 min with 0:100 of ethanol:water ratio

REFERENCES

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