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Easy method to prepare highly active N-doped carbon nanotube catalysts for advanced oxidation processes

Carbon materials are widely used as catalyst supports, but their use as catalysts is attracting a great deal of attention [1], in particular, N-doped carbon nanotubes (N-CNTs), since doping with N was shown to improve the catalytic performance in oxidation reactions [2]. In this work an easy to handle, solvent-free post-doping method was developed, which allows the incorporation of N-groups into the multi-walled carbon nanotube sp2 network, namely, quaternary nitrogen, pyrrolic and pyridinic groups. The method combines a mechanical treatment under ball-milling followed by thermal treatments under inert atmosphere or ammonia. Different vibration frequencies under ball milling, nitrogen precursors (melamine, urea), precursor/CNTs ratios, O-containing surface groups and final temperatures of the thermal treatment were evaluated towards the generation of active and stable N-species. The materials were characterized in terms of texture and surface chemistry by several techniques: N_2 adsorption, XPS, TPD, TGA and elemental analysis.

The catalytic performance of the novel N-doped CNTs was evaluated in two distinct advanced oxidation processes (AOPs): catalytic ozonation (COZ) and catalytic wet air oxidation (CWAO), using oxalic acid and phenol as model pollutants. These catalytic experiments were carried out in laboratory scale reactors. Figure 1 illustrates the catalytic results of oxalic acid oxidation by CWAO obtained with selected samples: pristine carbon nanotubes (CNT-O), ball-milled carbon nanotubes (CNT-BM) and CNT-BM sample functionalized with melamine (CNT-BM-M). The presence of N-containing surface groups improves the removal of the pollutants in both processes. Catalysts performance is influenced by the nature of the N-precursor, final temperature applied, ratio N-precursor/CNT, and eventual presence of acidic O-containing groups.

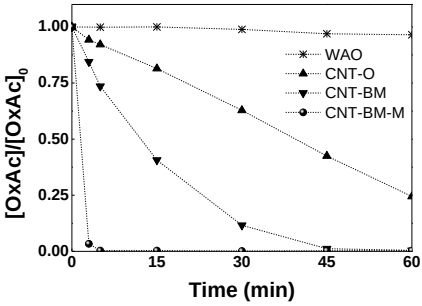

Figure 1: Dimensionless concentration of oxalic acid during CWAO.

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