

PhD subject

Elaboration and Characterization of Carbon Nanotubes and Alumina/Carbon Nanotubes Nanohybrids-Supported Catalysts for Water Treatment

Middle East as well as European directives encourage countries to protect and restore the quality of their water resources to achieve good chemical and ecological status. In general, several actions are necessary to maintain or improve the quality of water resources: protection against pollution by domestic wastewater and industrial discharges, reducing diffuse pollution from agriculture, protect groundwater, encourage water users to moderate their consumption and less pollution ... This social and industrial movement has also been accompanied over the last fifteen years, by an increase of scientific activity for any possible ecological depollution (water, air).

The field of nanotechnology offers more and more alternatives and catalysts supported on carbon nanotubes have shown more interesting capacities than the traditional technologies for water treatment. CNTs are one of the most intensively studied classes of nanomaterials because of their potential use in various fields of applications. The main objective of this thesis is to develop new catalysts supported on carbon nanotubes for application in the catalytic reduction of nitrate in drinking water without the production of ammonium. The choice of CNT is dictated by the exceptional properties of this material such as its high surface area, very good electrical conductivity, high adsorption capacity and the existence of a rich chemistry for its functionalization. Moreover, the combination of carbon nanotubes with other materials makes it possible to prepare nanohybrids having properties superior to those of materials taken separately due to the interaction between the two phases.

Studies of nitrate reduction have demonstrated that bimetallic catalysts are more efficient in comparison to monometallic. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru or Rh, and a transition metal, such as Cu, Sn, Ag, Ni, Fe or In on different supports (alumina (10,11,12,13), silica (14,15), titania (16), activated carbon (17), ceria (18), tin oxide (19), polymers (20), zirconia, titania and alumina membranes (21)). Among them, Pd-Cu, Pd-Sn and Pt-Cu were the most studied catalysts and have been considered as the most actives and selective for nitrate reduction, but are still inadequate in terms of selectivity towards nitrogen. It has been demonstrated that different supports significantly affect the catalytic activity and selectivity of the catalysts for nitrate reduction in addition to several other factors, such as: the reaction conditions, the catalysts preparation, the way the noble metal is promoted and the catalyst supported. These studies suggest that the support plays an important role in nitrate reduction. Constantinou et al (22) reported that the catalytic performance of Pd-Cu catalysts supported on various mixed metal oxides, $MO_x/\gamma-Al_2O_3$ ($MO_x = CeO_2, SrO, Mn_2O_3, Cr_2O_3, Y_2O_3$ and TiO_2), varies significantly depending on the support. Yoshinaga et al. (23) observed that a Pd-Cu catalyst supported on activated carbon is slightly more active than that supported on silica, more active than on alumina, and is the most selective to nitrogen.

Carbon nanotubes and nanofibers constitute a new family of support offering a good compromise between the advantages of activated carbon and high surface area graphite (28). Additionally, compared to conventional supports, CNT have a high flexibility for the dispersion of the active phase since it is possible to: (i) modulate their specific surface area or their internal diameter; (ii) easily functionalize chemically their surfaces; (iii) change their chemical composition; and (iv) deposit the catalytic phase either on their external surface or in their inner cavity (29).

In this context, the aim of this thesis is the development of innovative materials for the decontamination of polluted water.

Objectives

To develop efficient and stable catalysts supported on carbon nanotubes for nitrate removal in water with high selectivity to nitrogen. To the best of our knowledge, there is only one study using CNT as a support in the scope of this reaction (30,31,32).

- 1. To assess the influence of the CNT preparation method and surface chemistry on the on the characteristics of the catalysts including their catalytic performances.**
- 2. To combine the carbon nanotubes with other materials that make it possible to prepare nanohybrids having properties superior to those of materials taken separately due to the interaction between the two phases. Alumina is the material of choice to constitute a nanohybrid with carbon nanotubes.**
- 3. To assess the most promising metal phases supported on the nanohybrid and to optimize the metals compositions, for the catalysts with the best performances.**

Work Plan

- 1. Functionalization of CNTs by chemical method;**
- 2. Synthesis of CNT/Alumina nanohybrids by sol-gel process;**
- 3. Preparation of various bimetallic catalysts Pd-Cu; Pd-Pt; Pd-Sn on the synthesized nanohybrids supports;**
- 4. Study of the reduction of nitrates on thus developed catalyst;**
- 5. Study of the photodegradation of organic pollutants on thus developed catalyst;**

Encadrants

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