

Preparation and characterization of nanomaterials based on bifacial carbon nanotubes and iron oxides: Application in catalysis

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Abstract. The application of magnetic particles technology for the development of new nanomaterials has received considerable attention in recent years. In this context, the objective of this study is firstly, to prepare new catalytic materials that gather the strong adsorption capacities of carbon nanotubes and magnetic properties of iron, it concerns nanocomposites based on a mixture of carbon nanotubes in a very small amounts and iron oxide. Secondly we want to appear their capacities in catalytic oxidation reactions of phenol. Synthesis under the optimal conditions was carried out at different pH. And the characterization of this new nanomaterial reveals a good specific surface area BET, the identification of carbon nanotubes within the matrix was performed by infrared spectroscopy and transmission electron microscopy. The use of this new material as a catalytic support in catalytic oxidation reactions of phenol indicates the high selectivity of this latter and a yield better than this obtained with iron oxide supported by activated carbon. The good catalyst regeneration of the new catalysis and the improvement in their properties are the interesting parameters for the new type nanomaterials.

1. INTRODUCTION

Since the discovery of carbon nanotubes by Iijima in 1991 [1], research has focused on these new nanomaterials known by their electronic, mechanical and thermal properties. [2], The introduction of carbon nanotubes to polymers and other organic and inorganic molecules can acquire new properties for several applications such as microelectronics, energy storage, rechargeable batteries etc.

Recently, a new generation of materials for catalysis have been developed by insertion of new compounds with additional properties such as metallic groups at magnetic character [3], In this context, several metals were used such as Ni, Cu [4], Pt [5], Fe and Co [6], and particles oxides of SiO₂ [7], SnO₂ [8], Al₂O₃ [9] and TiO₂ [10], which are deposited on the surface of nanotubes.

Several studies have shown that the use of iron oxide supported on carbon nanotubes as catalyst present an industrial and environmental interest.

On the other hand, aqueous effluents contaminated by organic matter from the chemical industry and agricultural activity, are less biodegradable because of the high concentration of pollutant (COD of 500 mg to 1500 mg / L). The harmful effects of pollution by phenols lead to degradation of fauna; flora and fish, especially species at patty chain (eel, salmon, trout) accumulate phenols and may contain more than 30 mg / kg, then are so inedible. Oxidation processes in the liquid phase seems to offer an effective and less expensive solutions. On this principle, Alejandre and al [11, 12] studied the catalytic activity of copper and nickel in the oxidation reaction of phenol in aqueous medium, they showed that these catalysts are highly active in oxidation. The conversion rate of phenol depends on the catalyst preparation and the oxidation reaction is very selective in CO₂. Catalysts based

on heavy metal supported onto clays (montmorillonite) [13], silica [14] showed a high catalytic activity in oxidation of phenol by hydrogen peroxide. At atmospheric pressure and temperature of to 80 °C, phenol degradation is fast (15 min) and total with a mineralization selectivity of 93-59%. Original study on the treatment of a phenolic solution on heterogeneous phase by hydrogen peroxide with Fe-ZSM-5 catalyst was carried out by Fajerweg and al [15]. At 90 °C under atmospheric pressure a total elimination of phenol was recorded.

2. MATERIALS AND METHODS

Nanotubes of carbon are synthesis in the Carbon nanotubes: were synthesized at interuniversity Center for Materials research and engineering in Toulouse by the process Catalytic Chemical Vapor Deposition, after extraction, they are stored in wet form.

2.1. Preparation of nanocomposites

The preparation of materials DWCNT/ iron oxide was carried out as follows: A mixed solution of 0.1 M hexahydrate ferric chloride and 0.05 M tetrahydrate ferrous chloride with a molar ratio equal to 1/2. Different amounts of carbon nanotubes biface were added to the previous solution. At a temperature of 70 °C and at constant perimeter, a solution of NH₄OH 5M was introduced dropwise to precipitate iron oxides.

2.2. Preparation of catalysts

All catalysts were prepared by impregnation. The impregnation solution FeCl₃.6H₂O (volume equal to the pore volume: 2 ml) was added drop by drop to

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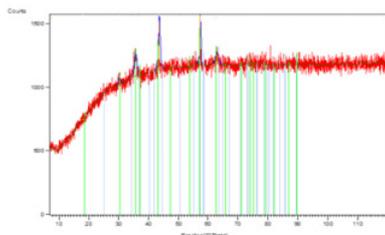


Figure 1. Spectrum DRX of DWCNT/iron oxide.

the support. The concentration of the solution was calculated in condition that the carbon supports are loaded by 10% and 20% of metal.

3. CHARACTERIZATION OF NANOMATERIALS

3.1. Analyse with DRX

The XRD spectrum obtained is comparable to the spectrum obtained by Xianjia Peng and al [15], the peaks correspond to different crystal structures of iron oxide and CNT. The peaks corresponding to diffraction angles $2\theta = 43.56^\circ$ and 57.27° are assigned to the structure of the double walled carbon nanotubes. The peaks corresponding to diffraction angles $2\theta = 35.65^\circ$, 62.97° and 30.18° are assigned to different types of iron oxides: Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The figure illustrated the spectrum DRX of DWCNT/iron oxide.

3.2. Specific surface measurement

Specific surface of oxide powders was performed with an automatic Micromeritics Flow Sorb II 2300, by nitrogen adsorption at the temperature of liquid nitrogen. Samples were degassed for 1 hour at 120°C .

3.3. Transmission electron microscopy

The powders were dispersed to be observed by ultrasound (tank) in ethanol. Few drops of the suspension were deposited on a grid of copper sample holder with a carbon film pierced with holes (Lacey). CNTs are observed at the holes in order to avoid interference with the carbon film.

3.4. Magnetic properties of CNT/iron oxide

We determined the Curie constants at different temperatures using the following formula

$$\chi P = C/T$$

χP is the paramagnetic susceptibility, C the Curie constant and T; Temperature in $^\circ\text{C}$.

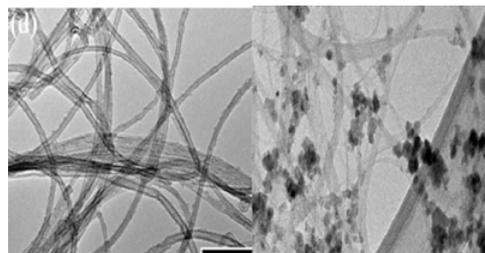


Figure 2. Micrographes TEM at 50 nm a) crude DWCNT b) DWCNT/iron oxide.

4. OXIDATION REACTION OF PHENOL

4.1. Experimental procedure

The reaction of phenol oxidation is performed in batch system. For a volume of 100ml of a 5.10^{-4}M phenol solution, we added a known quantity of washed catalyst. The beginning of oxidation reaction under standard conditions (C.N.T.P) correspond to the added of oxidizing agent (H_2O_2 5ml of 10^{-3}M). Samples were taken at known interval time in order to follow the evolution of pH, oxidant concentration, phenol.

4.2. Analytical techniques

The determination of hydrogen peroxide in stock solutions having concentrations up to 10^3M , released using the iodometric method. For concentrations between 10^{-5}M and 10^{-3}M , Eisenberg method is used [14]. The quantification of Iron is performed by atomic absorption. The derivate products are analyzed by liquid chromatography HPLC high pressure.

5. RESULTS AND DISCUSSION

5.1. Characterization of the nanocomposites

- Analysis by Transmission Electron Microscopy:

The following figures show the TEM pictures taken at two different magnifications, we see clearly the globules of iron oxide fully inserted between the wires of nanotubes at different magnifications.

Moreover, Iron oxides cover well the nanotube surface throughout its length, this is confirmed in reference [17].

In the figure a, we see clearly the wires of bifacial nanotubes in the absence of iron oxide.

- Specific surface area

The specific surface area was estimated at $259.91\text{m}^2/\text{g}$ while the pure CNTs have a specific surface of $335.5\text{m}^2/\text{g}$, the introduction of CNTs to iron oxides used to prepare materials with specific surface areas fairly significant.

- Magnetic properties

The Curie constant determined at 200°C showed that it remains constant with a value of 4.43 and 4.41 before and after reaction of oxidation respectively.

The iron chloride in the water gives Cl^- whose electronic structure without magnetic moment. Fe^{3+} ions

have five electrons in the layer 3d, then a layer incomplete and a nonzero magnetic moment and behave like the molecules of an ideal gas and therefore fall within the framework of the theory which neglects the interaction between the magnetic moments.

Finally, that nanomaterials retain their properties after use in catalysis, however this study are preliminary and must be considered part of a more rigorous with large scale of temperature.

5.2. Oxidation reaction

The purpose of this reaction is just to test the catalytic activity of synthesized nanocomposites.

The derivate products of the oxidation were analyzed by HPLC. The results are shown in the figure below.

Toward these results we observed that the phenol was oxidized to 99% in 60 min, the kinetics is very fast in the first minutes, and then stabilizes to reach equilibrium state after one hour. The amount of the consumed H_2O_2 varies in a manner proportional to the amount of phenol oxidized until the complete exhaustion of the oxidizing agent. HPLC analysis showed that there is formation of several derivates products; the final product of the oxidation is oxalic acid. In order to confirm the obtained results in the presence of solid catalyst in aqueous media and show clearly that oxidation was not due to the release of iron in the solution, a catalytic blank test is performed in homogeneous phase, in the same conditions as in the presence of the oxidation catalyst. 1 mg of iron is introduced in the form of ferric iron nitrate.

The results show that the rate of phenol eliminated in homogeneous oxidation does not exceed 20%. Finally, we can conclude that the obtained results in the presence of solid catalyst show that the oxidation reaction happens mainly in heterogeneous phase and this because of the stability and activity of the catalysts.

The study of the influence of the amount of iron in the nanocomposite on the yield of the reaction would be interesting.

6. CONCLUSION

Carbon nanotubes could confer to iron oxides very interesting properties as a catalyst with high activity, this is confirmed by the strong performance of oxidation and removal of phenol which is almost complete. The amount of CNT introduced is very small, which seems very interesting from an economic perspective. Several parameters are studied to prove the efficiency of such catalysts enhanced by carbon nanotubes. Finally, it is concluded from the environmental point of view, phenol oxidation is the most effective method for its removal and this kind of new materials is very promising since it can be easily regenerated and re-used by removing phenol through appropriate techniques.

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