PHOTOCATALYTIC PROPERTIES OF NOVEL ACTIVATED CARBONS OF HIGH SURFACE AREA DOPED WITH TIO₂ NANOPARTICLES

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Introduction

It is widely known the ability of titanium oxide (TiO_2) to act as a photocatalyst in different reactions [1], including the hydrolysis of water to produce hydrogen. Investigations developed in recent years show that the use of supports of carbon materials (activated carbons, nanotubes, etc.) increases the catalytic capacity of the titanium oxide [2]. In this context, the preparation of carbon materials from a new industrial coal, obtained from anthracene oil, has been the focus of the research [3]. This work is part of a wider project addressed to biomimetric catalysts development for fine chemistry, environment and energy applications. The preparation of activated carbons of high surface area (>3500 m^2/g) has been successfully carried out at 700ºC using KOH as activating agent. It has been studied the doping of this carbon with TiO_2 by incipient wetness impregnation method for application as a photocatalyst in the degradation reactions of phenol in water.

Experimental

Raw material: An anthracene oil-based pitch with a mesophase content of >99% (MAO).

Activated carbon preparation: The activation of the sample was carried out with KOH at 700 °C in a proportion of sample/KOH of 1:5. The activated carbon was called CM and was characterized by elemental analysis, electrical conductivity, physical adsorption and temperature programmed desorption.

Supported catalysts were prepared by incipient wetness impregnation of activated carbon using a solution of titanium tertbutoxide in toluene (30 wt. % TiO_2). After carbonization at 400 ºC the final amount of TiO_2 in the activated carbon (CMTi20) was of 20 wt. % as determined by using a thermobalance in air atmosphere at 1000 ºC.

Activated carbon characterization: The textural characteristics of the samples were analyzed by means of N_2 adsorption at 77 K in an ASAP 2020 Micromeritics equipment using around 100 mg of sample in each experiment. Before the experiments, the samples were outgassed at 350ºC for 10 h under vacuum (pressure below 10^{-3} Pa).

The pores were classified according to IUPAC recommendations into micropores (< 2 nm width), mesopores (2-50 nm width) and macropores (> 50 nm width). The apparent surface area was determined from the N_2-adsorption isotherm using the BET equation. The total micropore volume (Vmicro) was calculated by applying the Dubinin-Radushkevich equation to the N_2 adsorption isotherms, and the total pore volume was obtained from N_2 adsorption when P/Pº = 0.99. The volume of mesopores (Vmeso) was calculated by subtracting the total micropore volume (Vmicro) from the total pore volume (Vtotal). The microporous surface area was obtained from the equation: Smic(m^2g^{-1}) = 2000 Vmicro (cm^3g^{-1})/L_0 (nm), where L_0 represents the average micropore width. The pore size distribution was obtained by the density function theory (DFT).

The photocatalitic degradation of phenol was studied in a stirred quartz reactor of 250 mL equipped with temperature control to maintain a constant temperature (25 ºC). The system also included an ultraviolet lamp (UV) of 200W. Initial concentration of phenol solution was 10^{-3} M (200 mL). Amounts of 50 and 100 mg of catalyst were used (noted as CMTi20-50 and CMTi20-100 respectively). The reaction was carried out without light during the first 15 min. After this time a pre-warmed lamp was placed inside the reactor. The quantity of phenol in the water was determined by high performance liquid chromatography (HPLC) using UV detector.

Results and Discussion

Chemical activation of anthracene oil-based pitch with at a 1:5 ratio of sample:KOH ratio at 700 ºC, leads to an activated carbon (CM) with a surface area of SBET ~ 3500 m^2g^{-1} and a well developed micro and mesoporosity (Table 1).

Table 1. Textural characteristics of the parent activated carbon CM and activated carbon containing 20% TiO_2 (CMTi20).

	CM	CMTi20
SBET (m^2g^{-1})^a	3499.5	2666.2
Vmicro (cm^3g^{-1})^b	1.0	0.8
Vmeso (cm^3g^{-1})^c	0.9	0.6
Vtotal (cm^3g^{-1})^e	2.0	1.4
L_0 nm^e	1.9	1.7

^{a}"apparent" surface area BET, ^{b} micropore volume, ^{c} mesopore volume, ^{d} total volume of pores, ^{e} pore diameter

Doping of CM with TiO_2 (20 wt.%) led to a sample (CMTi20) exhibiting homogeneous dispersions of the oxide along the activated carbon surface, as confirmed by the analysis of the sample by means of scanning electron image (SEM) with energy dispersive X-ray microanalyses (EDX) (Figure 1).
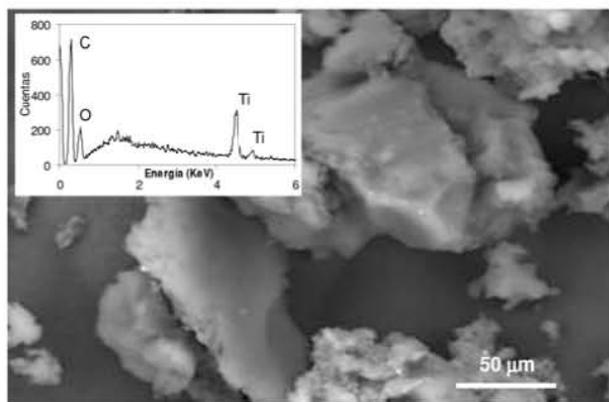
Fig. 1 Scanning electron image (SEM-EDX) of the activated carbon containing 20% TiO_2 (CMTi20).

Compared to the parent CM, the analysis of the textural characteristics of CMTi20 confirmed a decrease in the SBET down to a value of $\sim$ 2600 m^2/g. This is related with a decrease in the volume of mesopores and micropores. As a possible explanation, clogging of the micropores while the oxide is being introduced.

The photocatalytic activity of CMTi20 was studied in relation to the degradation of phenol in water. For this purpose, a solution of phenol and water (10^{-3} M) was used. Amounts of 50 and 100 mg of CMTi20 were tested in this study (CMTi20-50 and CMTi20-100 respectively). The results obtained are shown in Figure 2.

The adsorption properties of the activated carbons due to their porosity were first studied. For this purpose, the adsorption reaction was initiated in the darkness. Equilibrium of adsorption of phenol on the activated carbon surface was achieved in both cases after 15 min. The adsorption of phenol at this point was 6.8 x 10-4 mol/L for CMTi20-50 and 5.7 x 10-4 mol/L for CMTi20-100.

Photocatalytic degradation of the phenol was then analyzed. After 2 hours, the photocatalysis reaction produced a decrease in the concentration of phenol of 57% for CMTi20-50 and of 85 wt.% for CMTi20-100 (Figure 2). The concentrations of phenol at these points were 4.15 x 10^{-4} M and 1.57 x 10^{-4} M respectively. The effectiveness of the activated carbons in the photocatalytic degradation phenol was thus demonstrated.
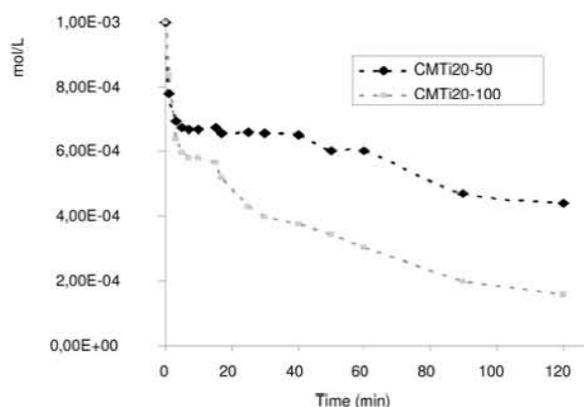
Fig. 2 Variations of the phenol concentrations with time for amount of catalyst of 50 mg (CMTi20-50) and 100mg (CMTi20-100).

Conclusions

Anthracene oil-based pitch was successfully activated with KOH to produce highly porous activated carbons (SBET: $\sim$ 3500 m^2/g). Doping of this carbon with TiO_2 in a 20 wt.% led to homogeneous dispersions of the catalyst over the activated carbon surface. This process reduced the meso and microporosity of the activated carbon and led to a sample, CMTi20, with a SBET of $\sim$ 2600 m^2/g.

The photocatalytic activity of CMTi20 in the degradation of phenol in water has been demonstrated. After the a previous adsorption of the phenol by the porosity during the first 15 min. a decrease in the concentration of phenol after 2 hours of 57% for CMTi20-50 and 85% for CMTi20-100 was observed.

References

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