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The influence of surface chemistry of activated carbons on the selective decomposition of hydrogen peroxide

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Activated carbons can act as metal free catalysts on wet peroxide oxidation to generate $HO^\bullet$ radicals by means of H_2O_2 decomposition. To quantify the yield of $HO^\bullet$ formed ($Y_{HO^\bullet}$) the consumption of H_2O_2 and the oxygen formation were measured in experiments performed with and without an $HO^\bullet$ scavenger. After 150 min of reaction, at T = 323 K, pH = 3 and catalyst load = 0.1 g L^{-1}, the highest $Y_{HO^\bullet}$ was obtained for the catalyst with higher basicity, obtained from the successive modification of the original activated carbon with nitric acid, hydrothermal treatment with urea and thermal treatment with N_2. A linear correlation between $Y_{HO^\bullet}$ and the concentration of basic active sites was obtained.

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The influence of surface chemistry of activated carbons on the selective decomposition of hydrogen peroxide

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1 Introduction

Hydrogen peroxide (H_2O_2) is currently used in advanced oxidation processes (AOP) for wastewater treatment, such as catalytic wet peroxide oxidation (CWPO). This process consists in a liquid phase remediation solution involving the use of a suitable catalyst to promote H_2O_2 decomposition and consequent formation of highly reactive hydroxyl radicals ($HO^\bullet$) which are powerful oxidizing species exhibiting a higher oxidation activity than other conventional oxidants [1]. Recently, it has been shown that activated carbon materials can act as metal-free catalysts for the CWPO of organic pollutants in aqueous solutions [2, 3]. Although the H_2O_2 decomposition mechanism is quite complex, involving the generation of various intermediate species, including the formation of $HO^\bullet$ [4, 5], it is of utmost importance to quantify the ability of activated carbons to promote the decomposition of H_2O_2 via formation of $HO^\bullet$, a key step to optimize the efficiency of the CWPO process. In the present work, the influence of the surface chemistry of activated carbons on the catalytic decomposition of H_2O_2 was assessed by determining the yield of highly reactive $HO^\bullet$ formed in CWPO. For that purpose, the original activated carbon (AC) was modified in order to produce a set of materials with a wide range of chemical characteristics.

2 Experimental

Modified activated carbons

AC (Norit ROX 0.8) was ground to particle sizes ranging from 0.106 mm to 0.250 mm, being afterwards subjected to several chemical modifications: liquid phase treatment with concentrated sulphuric acid at 423 K (ACS); nitric acid oxidation at boiling temperature (ACN), followed by hydrothermal treatment with urea at 473 K (ACNU) and a gas-phase thermal treatment at 873 K under a N_2 flow (ACNUT). Each treatment produced materials with different surface chemistry (pH_{PZC} values ranging between 1.6 and 10.3), without significant modification of the original textural properties. ACS was found to be the most acidic material, with sulphur containing functional groups at the carbon surface [3] and ACNUT was the material with the most markedly basic character, with nitrogen containing functional groups at the carbon surface [6].

H_2O_2 decomposition experimental procedures

Two distinct experimental procedures were considered in this work: experiments where the concentration of H_2O_2 was followed, and experiments where the amount of oxygen formed was followed, either with or without the presence of methanol (20 g L^{-1}), which acts as scavenger of $HO^\bullet$. In both experimental procedures, the H_2O_2 decomposition reactions were performed in a 500 mL well-stirred (600 rpm) glass reactor, equipped with a condenser, a temperature measurement thermocouple, a pH measurement electrode and a sample collection port. The reactor was loaded with 250 mL of distilled water and heated by immersion in a water bath with temperature control. Upon stabilization at the desired temperature, the solution pH was adjusted by means of H_2SO_4 and NaOH solutions (1.0 mol L^{-1} and 0.02 mol L^{-1}). The experiments were carried out during 150 min at T = 323 K, pH = 3, catalyst load = 0.1 g L^{-1} and an H_2O_2 concentration of 34.6 mmol L^{-1}. The H_2O_2 concentration was followed by a colorimetric method and the oxygen formed was monitored by a volumetric glass system.

3 Results and discussion

The yield of $HO^\bullet$ formed during the H_2O_2 decomposition process was obtained considering the simplified mechanism for H_2O_2 decomposition shown in equations 1 to 4 [5, 7, 8], where S^+ and S represent, respectively, oxidized and reduced active sites existing at the carbon surface. When using methanol (MeOH) as $HO^\bullet$ scavenger, the H_2O_2 decomposition mechanism proceeds as described in equations 1, 2 and 5. Therefore, the amount of $HO^\bullet$ formed can be determined by the difference between the oxygen formed during the H_2O_2 decomposition experiments performed with and without MeOH and the corresponding yield of $HO^\bullet$ formed ($Y_{HO^\bullet}$) is thus obtained dividing the amount of $HO^{\bullet}$ formed by the H_2O_2 consumed during the H_2O_2 decomposition process, which is equivalent to the maximum amount of $HO^{\bullet}$ that could be formed from the effectively decomposed H_2O_2 (Eq. 2).

$$H_2O_2 + S^+ \rightarrow [HOO^{\bullet} + H^+ + S] \rightarrow \tfrac{1}{2}O_2 + H_2O + S^+ \tag{1}$$

$$H_2O_2 + S \rightarrow HO^{\bullet} + OH^- + S^+ \tag{2}$$

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HOO^{\bullet} \tag{3}$$

$$HO^{\bullet} + HOO^{\bullet} \rightarrow H_2O + O_2 \tag{4}$$

$$HO^{\bullet} + MeOH \rightarrow \text{Products} \tag{5}$$

In preliminary H_2O_2 decomposition experiments, AC, ACS and ACNUT were the most active catalysts amongst all tested materials. These were selected for further studies on the mechanistic interpretation of H_2O_2 decomposition via $HO^{\bullet}$ formation (Figure 1a) and the respective $Y_{HO^{\bullet}}$ were determined (Figure 1b). The highest $Y_{HO^{\bullet}}$ was obtained when using ACNUT as catalyst, with the corresponding values following the order ACS < AC < ACNUT. This order is in accordance with the concentration of basic active sites at the surface of these materials, suggesting that the basicity of carbon materials increases the yield of $HO^{\bullet}$ formation, as clearly visible when $Y_{HO^{\bullet}}$ is plotted against the concentration of basic active sites at the surface of the carbon materials (*cf.* Figure 1b), where the existence of a linear correlation becomes evident.

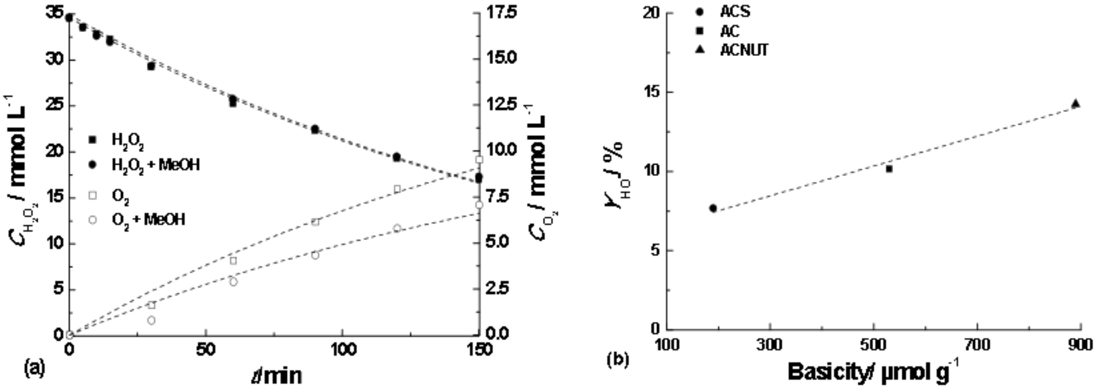

Fig. 1. (a) H_2O_2 decomposition (filled symbols) and oxygen formation (open symbols) during the H_2O_2 decomposition experiments with ACNUT; (b) $Y_{HO^{\bullet}}$ obtained after 150 min of reaction as function of the concentration of basic active sites.

4 Conclusions

The proposed reaction mechanism for decomposition of H_2O_2, leading to the formation of $HO^{\bullet}$ as main oxidative agent, is in line with experimental data. The yield of $HO^{\bullet}$ formation is proportional to the surface basicity of the catalyst. Accordingly, ACNUT – an activated carbon material with a markedly basic character – led to the highest yield of $HO^{\bullet}$ formed during the H_2O_2 decomposition process (above 14%).

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