Preparation of activated carbon-metal (hydr)oxide photocatalysts under different heating conditions. Chemical aspects.

Preparación de fotocatalizadores carbón activado-(hydr) oxidos metálicos en diferentes condiciones de calentamiento. Aspectos químicos.

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Abstract

This study deals with the preparation of activated carbon (AC)-metal (hydr)oxide (MO) photocatalysts from commercial AC and Al^{3+}, Fe^{3+}, Zn^{2+}, $SnCl_2$, TiO_2 and WO_4^{2-} in water, with special emphasis on the chemical changes produced along the process. Overall, three series of samples were obtained by first soaking at 80 ºC and oven-drying at 120 ºC (S1) and by subsequent heating at 200 ºC (S2) or 850 ºC (S3) in N_2 atmosphere. pH of the impregnation solution/suspension was 2.91 with Al^{3+}, 1.54 with Fe^{3+}, 5.16 with Zn^{2+}, 1.37 with $SnCl_2$, 5.84 with TiO_2 and 9.54 with WO_4^{2-}. Data of the process yield at the three temperatures and of the ash content are reported. For S1, yield varies by $SnCl_2 >> Fe^{3+} > WO_4^{2-} > Zn^{2+} = TiO_2 > Al^{3+}$.

Resumen

Se estudia la preparación de materiales de carbón activado (AC)-(hydr)oxide de metales (MO) a partir de un carbón activado comercial y de Al^{3+}, Fe^{3+}, Zn^{2+}, $SnCl_2$, TiO_2 y WO_4^{2-} en disolución/suspensión acuosa, con especial énfasis en los cambios químicos producidos a lo largo del proceso. En total se han preparado tres series de muestras mediante remojo at 80 ºC y secado en estufa a 120 ºC (S1) y posterior calentamiento de estas muestras bien a 200 ºC (S2) o a 850 ºC (S3) en N_2. El pH del líquido de impregnación fue 2.91 con Al^{3+}, 1.54 con Fe^{3+}, 5.16 con Zn^{2+}, 1.37 con $SnCl_2$, 5.84 con TiO_2 y 9.54 con WO_4^{2-}. Se aportan los datos del rendimiento del proceso y el contenido de cenizas de las muestras. Para las muestras de la serie S1, el rendimiento del proceso varía según $SnCl_2 >> Fe^{3+} > WO_4^{2-} > Zn^{2+} = TiO_2 > Al^{3+}$.

1. Introduction

The technological and economic importance of photocatalysis has increased considerably over the past decades because of the practical interest in air and water remediation, self-cleaning surfaces, self-sterilizing surfaces, and hydrogen generation using green energy of sunlight [1]. In 2009 the global market for photocatalytic products was $848 million and with an annual growth rate of 14.3 % a global volume of $1.7 billion was expected in 2014 [2]. TiO_2 is by far the most frequently employed photocatalyst, owing to the advantages of earth abundance, low toxicity, and thermal and chemical stability, besides being cheap, insoluble under most conditions, and photostable [3]. In photocatalytic reactions, metal oxides are generally suspended in the liquid phase or dispersed over high-surface-area materials. The former process is handicapped by filtration of TiO_2 fine particles and effective absorption of ultraviolet-visible radiation. In the latter process, activated carbon has been extensively researched and used as a support for TiO_2 [4]. Semiconductor metal oxides are not only TiO_2 but also Al_2O_3, Fe_2O_3, ZnO, SnO_2, and WO_3. The preparation methods and applications for these metal oxides supported on AC were critically reviewed before [5]. Here, mainly for comparison purposes (see Ref.: 6-8), the chemical and mass changes originated as a result of the impregnation process of AC with Al^{3+}, Fe^{3+}, Zn^{2+}, $SnCl_2$, TiO_2 and WO_4^{2-} in water and of the subsequent heat treatment of the resulting products are examined.

2. Experimental

Table 1. Preparation of the AC-MO catalysts.Yield and ash content.
Tabla 1. Preparación de los catalizadores AC-MO. Rendimiento y contenido de cenizas.

Series	Sample	Yield / wt%	Ash content / wt%
	AC	-	4.72
S1	A120	102	7.11
	F120	114	13.63
	Z120	103	9.73
	S120	149	27.31
	T120	103	8.82
	W120	106	9.46
S2	A200	93	8.86
	F200	94	13.55
	Z200	91	9.45
	S200	96	27.21
	T200	96	8.05
	W200	96	9.93
S3	A850	90	5.68
	F850	81	14.66
	Z850	84	6.18
	S850	68	2.34
	T850	98	9.33
	W850	95	11.54

Activated carbon (AC) from Merck (1.5 mm average particle size) and $Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ (Panreac; reagent grade), and anatase powder (Aldrich; particle size lower than 44 µm) in water were used in the preparation of the AC-MO. pH of the impregnation solution was in turn 2.91, 1.54, 5.16, 1.37, 5.84 and 9.54. The preparation of the samples was undertaken by wet impregnation in two successive soaking (80 ºC, 5 h) and oven-drying (120 ºC, 24 h) steps (S1) and subsequent heating at 200 (S2) or 850 ºC (S3) for 2 h in N_2 atmosphere. The yield of the process of preparation of the catalyst samples was estimated by the following expression:

$$Y(\%) = \frac{M_f(g)}{M_i(g)} \cdot 100 \qquad (1)$$

where M_i is the initial mass of AC or of the samples of series 1 and M_f is the final mass of product. The codes assigned to the catalyst samples are shown in Table 1, which also lists yield values. The ash content was determined by incineration of the samples at 650 ºC for 12 h. Composition data are also compiled in Table 1.

3. Results and discussion

3.1. Preparation of the samples

3.1.1. pH of the impregnation solution

In the preparation of the AC-MO materials from AC and Al^{3+}, Fe^{3+}, Zn^{2+}, $SnCl_2$, WO_4^{2-} or TiO_2 in water, the pH of the impregnation solution gives idea of speciation, which is an essential factor because it controls the loading process and as a last resort the mass change produced in AC. As shown in Table 1, the measured pH varies by $SnCl_2 <$ $Fe^{3+} <$ $Al^{3+} <$ water $\approx Zn^{2+} \approx TiO_2 <$ WO_4^{2-} and in the wide range between 1.37 for $SnCl_2$ and 9.54 for WO_4^{2-}. For the Al^{3+}, Fe^{3+} and Zn^{2+} ions, the pH variation is consistent with the tendency exhibited by these metal ions to undergo hydrolysis. Metal ions, especially in high oxidation state, in aqueous solution undergo hydrolysis by the reaction (2):
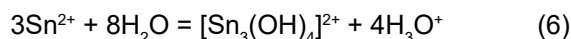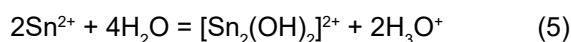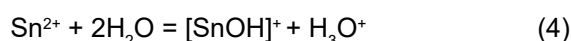
$$[M(H_2O)_n]^{z+} + H_2O = [M(H_2O)_{(n-1)}OH]^{(z-1)} + H_3O^+ \quad (2)$$
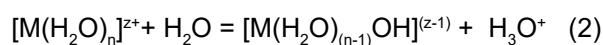
that for the sake of brevity this reaction is often written

$$M^{z+} + H_2O = [M(OH)]^{(z-1)} + H_3O^+ \qquad (3)$$
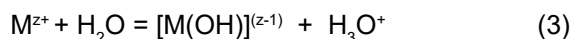
In this reaction, a proton from a water molecule in the coordination sphere of the metal ion is transferred to a water molecule in the solvent. The aquo-cation behaves as a Brönsted´s acid, whereas the water molecule does as a Brönsted´s base. As a result of the hydrolysis reaction, in general, metal ions in aqueous solution are found as metal aquo complexes and metal hydroxo complexes of formula $[M(H_2O)_n]^{z+}$ and $[M(H_2O)_{n-m}(OH)_m]^{(z-m)+}$, the chemical composition of these complexes being dependent on the solution concentration (i.e., 0.27 mol L^{-1} for Al^{3+}, 0.25 mol L^{-1} for Fe^{3+} and 0.34 mol L^{-1} for Zn^{2+}) and pH. The hydrolysis of Fe^{3+} begins at about pH 1 with formation of $[Fe(OH)]^{2+}$. Likewise, , the species $[Fe(OH)_2]^+$, $[Fe_2(OH)_2]^{4+}$, and $[Fe_3(OH)_4]^{5+}$ were indentified, usually at higher pH.

Al^{3+} can be hydrolyzed extensively to form solutions of polynuclear hydroxides complexes and very large polymeric or colloidal species. Mononuclear species $[AlOH]^{2+}$-$[Al(OH)_4]^-$ are also formed, the former appearing above pH 3. Zn^{2+} hydrolyzes only sparingly in acid media to produce $[ZnOH]^+$ and $[Zn_2OH]^{3+}$ before precipitation commences in the neutral region. In basic media, $[Zn(OH)_4]^{2-}$ and perhaps $[Zn_2(OH)_6]^{2-}$ are formed [9].

Although $SnCl_2$ is mainly covalent in nature the electronegativities of Sn, Cl and O indicate that the Sn-Cl and Sn-O bonds possess a relatively high ionic character and therefore $SnCl_2$ is readily soluble in water, i.e. 178 g of $SnCl_2$ in 100 g of water at 10 ºC [10]. Furthermore, it may take part in a number of equilibrium reactions depending on factors such as pH, concentration, presence of aerial oxygen, and storage time [9, 11-15]. First, in solutions at pH<2, the acidic cation Sn^{2+} easily hydrolyses by

$$Sn^{2+} + 2H_2O = [SnOH]^+ + H_3O^+ \qquad (4)$$

$$2Sn^{2+} + 4H_2O = [Sn_2(OH)_2]^{2+} + 2H_3O^+ \qquad (5)$$

$$3Sn^{2+} + 8H_2O = [Sn_3(OH)_4]^{2+} + 4H_3O^+ \qquad (6)$$

and Sn^{2+} hydroxichlorides are formed, the trimeric species being the predominant one [9, 11, 12]. In fact, the strength of Sn^{2+} as an aqueous acid is principally as a result of the rapid polymerization of the mononuclear conjugate base [13]. At pH near 2, $SnO \cdot H_2O$ should precipitate and transform into SnO. However, in the presence of chloride ion basic salts precipitate first [9, 12] and SnO is formed then at higher pH [14, 15]. Second, as the main hydrolytic species of Sn^{2+}, $[SnOH]^+$, $Sn(OH)_2$ and $[Sn(OH)_3]^-$ mononuclear species with diluted Sn^{2+} solutions (5 x 10^{-7} mol L^{-1}) and $[Sn_2(OH)_2]^{2+}$ and $[Sn_3(OH)_4]^{2+}$ polynuclear species for higher Sn^{2+} concentrations (10^{-3} and 2 x 10^{-2} mol L^{-1}) were also reported [16 and citations therein]. Third, $SnCl_2$ is a fair reducing agent that is slowly oxidized in aqueous solution by atmospheric oxygen [17]:

$$3SnCl_2 + 1/2O_2 + H_2O = SnCl_4 + 2Sn(OH)Cl \qquad (7)$$
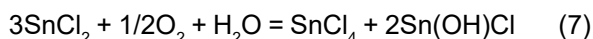
Because SnO_2 is a weak base, $SnCl_4$ in aqueous solution is hydrolyzed to considerable degree, substantially according to:

$$SnCl_4 + 2H_2O = SnO_2 + 4HCl \qquad (8)$$
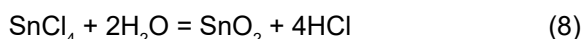
with the resulting white SnO_2 remaining in solution in colloidal form. Simultaneously, HCl to some extent combines with un-reacted $SnCl_4$ and hexachlorostannic acid, $H_2[SnCl_6]$, is formed [17]. Finally, during the storage of acidic $SnCl_2$ solutions, a small precipitate was gradually formed which became visible only after 30-45 days had elapsed since their preparation. After isolation, the precipitate was made up of the phases of Sn(II,IV) hydroxychlorides and other oxo- and hydroxo-complexes [18]. Needless

to say, the low pH of the $SnCl_2$ solution (i.e., 1.37) used in the impregnation of AC advocates for a predominance of reactions such as (4) and (8), because of a more favourable generation of HCl. In the case of the reaction (8), however, it should be taken into account that the presence of Sn^{4+} as colloidal SnO_2 in such a solution should be minor due to the low concentration of O_2 (i.e. presumably ~ 1.3 x 10^{-3} mol L^{-1} [18]) as compared to $SnCl_2$ (i.e. 0.44 mol L^{-1}) and also the slow kinetics of the reaction (7) [17]. As a result of the very short storage time of the $SnCl_2$ solution (in fact, it was used immediately after preparation) before using it in the impregnation of AC, in addition to un-reacted $SnCl_2$ and ions coming from its dissociation, it should primarily contain Sn^{2+} polynuclear species rather than Sn^{2+} and Sn^{4+} polymeric species.

After the $SnCl_2$ solution was brought into contact with AC, i.e. the measured pH of the point of zero charge (pH_{pzc}) for this carbon was as high as 10.50, at the onset of the soaking step, pH should increase because of the protonation of AC basic sites [19] and SnO should then be formed. The following reactions will account for the solubility of SnO in water in an acidic medium [9, 20]:

$$SnO(s) + H_3O^+ = [Sn(OH)]^+ + H_2O \qquad (9)$$

$$SnO(s) + 2H_3O^+ = Sn^{2+} + 3H_2O \qquad (10)$$
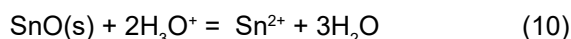
and therefore autoxidation likely went on by further embracing increased amounts of $[Sn(OH)]^+$ and Sn^{2+}. Stannnous oxide exhibits a high ability to oxidation and as a result special care was observed in its preparation to protect it from oxygen since the Sn^{2+} ion changes very rapidly to Sn^{4+} ion in the presence of atmospheric oxygen [20]. Of course, like for the $SnCl_2$ solution, the extent to which the oxidation process occurred during the soaking step was conditioned by the small amount of O_2 present in the medium. However, the opposite applies to the subsequent oven-drying step at 120 ºC, which was performed in air atmosphere and therefore without no restriction to the O_2 availability, apart from its low solubility. This is 3.08 cm^3 (gas at STP) in 100 cm^3 H_2O at 20 ºC [21], although in the $SnCl_2$ solution under the temperature conditions in the soaking step it should decrease not only because of the higher operating temperature (i.e. 80 ºC) but also because of the presence of various inorganic chemical species in the medium. However, relating to the presence of $SnCl_2$ in the medium, pH should not affect the O_2 solubility as Cl^- is the conjugate base of the strong acid HCl. During the oven-drying step, it is likely that at the beginning the sudden water evaporation from the wetted-freshly impregnated AC prevented O_2 from entering AC porosity and that, after a certain time had elapsed, the access of O_2 to AC porosity was favored because of the O_2 mobility and thereby diffusion ease at 120 ºC.

In connection with the autoxidation of $SnCl_2$ it was stated before that its study is complicated by the presence of a large number of ionic equilibria involving dissociation, hydrolysis and complex formation [22]. It is a thermal and photochemical chain reaction, showing peroxide formation, induced oxidation of other molecular species present in the solution, and great sensitivity to positive and negative catalysts. The complex $HSnCl_3$ or H_2SnCl_4 was described as playing an important role in the oxidation of $SnCl_2$ [23]. Furthermore, one such positive catalyst is activated carbon, which accelerated the reaction but not in proportion to the weight used [24]. Air-induced oxidation of organic and inorganic systems goes through free radical processes. Autoxidation reactions are usually subdivided into initiation, propagation and termination reactions. Two types of initial reactions can take place: abstraction of H atoms from various bonds and addition of O_2 to the free radical sites [25]. Molecular oxygen adds and gives peroxy radicals, yet O_2 can also act directly as an oxidant (i.e., electron acceptor) [26]. Since chemical species such as peroxides are stronger oxidants than molecular O_2 (i.e., as a guide, E^o is 1.776 V for H_2O_2 and 1.229 V for O_2 [10]), it can be presumed that in the autoxidation of $SnCl_2$ AC behaved simultaneously as a catalyst of the reaction and as a reactant that could also be oxidized.

Titanium dioxide (anatase) shows a high tendency to hydroxylation [27]. For hydrated titania obtained by hydrolysis of titanium salts it was assumed that its surface is completely hydroxylated. However drying, even at room temperature, leads to irreversible dehydroxylation [28]. Water adsorption on strongly dehydroxylated anatase takes place in two ways: part of the water molecules are dissociated forming hydroxyl groups again, while the major part of water is adsorbed molecularly [29]. Repetition of the hydroxylation and dehydroxylation cycles leads to a decreasing concentration of the sites for dissociative adsorption, probably owing to surface reconstructions [30]. Accordingly, it seems that after the contact with water already hydroxylated anatase only underwent a slight hydroxylation, in accord with the small pH change produced for the TiO_2 suspension in respect to deionized water.

According to the Pourbaix´s diagram for tungsten, the only ionic species stable in aqueous solution at basic pH is the tungstate ion, WO_4^{2-}; whereas the existence of pertungstic ion WO_5^{2-} remains hypothetical [31]. Because of hydration, structures such as $[WO_2(OH)_4]^{2-}$ and $[W(OH)_8]^{2-}$ were proposed as well for the WO_4^{2-} ion in aqueous solution at pH ≥ 6 [32]. The pH of 9.54 measured for the $Na_2WO_4.2H_2O$ solution falls within the range of pH values between 9.15 and 10.5 reported in the literature for molar solutions prepared from $Na_2WO_4.2H_2O$ and purified water [33]. The alkalinity of the WO_4^{2-} solution may be due to the presence of excess alkali (i.e., NaOH) in commercial $Na_2WO_4. 2H_2O$ or to Na_2WO_4 hydrolysis and polymerization in accord with the postulated basic mechanism in the formation of iso- and heteropolytungstates from WO_4^{2-} [33]:

$$nWO_4^{2-} + (n+1)H_2O = [H_{(n-1)}(WO_4)_n 2H_2O]^{(n+1)-} + (n-1)OH^- \qquad (11)$$
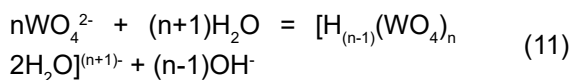
3.1.2. Yield

The yield of the impregnation process of AC for S1 data in Table 1 is higher than 100% for all samples and strongly dependent on the MO precursor. Thus,

it varies in the wide range between 102 wt% for A120 to 149 wt% for S120 by S120 >> F120 > W120 > Z120 = T120 > A120 and is markedly higher for F120 and very especially for S120 than for the rest of the samples belonging to S1. Probably, two important factors with influence on the process yield are the diffusion of the MO precursor in pores of AC and the metal density. Diffusion will be mainly dependent on the size of the MO precursor, which may be found as a hydrated, hydrolyzed or polymerized metal ion and also as a hydroxylated MO in the aqueous system. In the case of S120, mass balance is consistent with the involvement of small size tin species (e.g., Sn^{2+} and $[Sn(OH)]^+$), generated from $SnCl_2$, in the diffusion process and with their subsequent oxidation catalyzed by AC, which should ultimately give tin species with a high oxygen content such as SnO_2. For Fe^{3+}, polynuclear hydrolyzed species may be formed in the 0.25 mol L^{-1} solution by the reaction [34]:

$$2FeOH^{2+} = Fe_2(OH)_2^{4+} \qquad (12)$$

Likewise, WO_4^{2-} should transform into WO_3 by:

$$WO_4^{2-} + 2H^+ = WO_3 + H_2O \qquad (13)$$
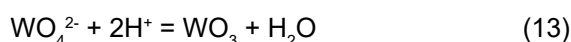
despite the high pH of the WO_4^{2-} solution and AC´s surface (i.e., pH of the point of zero charge is 10.5 for AC). Probably, the reaction (13) was favoured by the evaporation of water during the oven-drying step. Finally, from the low yield for T120 it is evident the influence of particle size on the impregnation process of AC. On the other hand, the latter is also an important factor in connection with the process yield because of the wide set of metal precursors used in the study. Density is a function of the metal atomic mass, which determines the weight of a given amount of sample and for the here used MO precursors it ranges between 26.981 for Al and 183.85 for W [33]. On the other hand, yield varies between 91-96 wt% for S2 and 68 - 98 wt% for S3, and therefore in a wider range for S3 than for S2.

3.1.3. Ash content

As can be seen in Table 1, for a large number of AC-MO samples, the ash content is about twice higher than for AC. For S850, however, it is noticeably lower than for AC. For S1, the ash content varies by S120 > F120 > Z120 > W120 > T120 > A120, the correlation with yield being as a rule good. The slightly different ash contents for homologous samples of S1and S2 argue for a reversible desorption of water and partial dehydroxylation of S1 in the preparation of S2, because of the 200 ºC-low heat treatment temperature. On the contrary, for S3 the ash content varies by F850 > W850 > T850 > Z850 > A850 > S850 and widely between 2.34 wt% for S850 and 14.66 wt% for F850. The ash content is low not only for S850 but also for A850 and Z850, whereas it is high for F850 and W850. Accordingly, it is attributable to the carbothermal reduction of M_nO_m:

$$M_nO_m + mC \rightarrow nM + mCO \qquad (14)$$

that originates CO release and M. Lower-melting point metals (i.e. Sn, 231.93 ºC; Zn, 419.53 ºC; Al, 660.32 ºC) will melt and vaporize, whereas higher-melting point metals (i.e. Fe, 1538 ºC; W, 3414 ºC) will remain unaltered in the samples. This influenced the ash content as both metals should be oxidized again to M_nO_m during the incineration process of the samples.

Conclusions

The preparation of AC-MO photocatalysts from AC and Al^{3+}, Fe^{3+}, Zn^{2+}, $SnCl_2$, TiO_2 or WO_4^{2-} in water has been thoroughly studied by taking into account the concentration and pH, and thereby speciation, of the impregnation solution. For S1, the process yield varies by S120 >> F120 > W120 > Z120 = T120 > A120 and ranges between 102 wt% for A120 and 149 wt% for S120. The mass changes as a rule are stronger for S1 and S3 than for S2. The ash content is higher for F120 and especially for S120 than for the remaining samples. A number of metal oxides are carbothermally reduced at 850 ºC and the resulting metal may melt and vaporize, depending on melting temperature relative to heat treatment temperature. The ash content becomes as low as 2.34 wt% for S850.

Acknowledgements

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