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PHOTOCATALYTIC ACTIVITY OF METAL DOPED TIO_2 AEROGELS PREPARED BY SOL-GEL PROCESS

M. POPA*, I.C. POPESCU, V. DANCIU

ABSTRACT. Oxide semiconductor photocatalyst based on TiO_2 is normally used in UV photodegradation of different organic pollutants. This paper is focused on preparation of 1at%Cu, 1at%Ce, 1at%Fe doped and undoped TiO_2 aerogels and their application in photodegradation of an organic compound. The aerogels were obtained by sol-gel process in acid catalysis, followed by supercritical drying with liquid CO_2. The preparation process involved a single precursor based on $Ti(OPr)_4$ and doping was made by using ethanolic solutions of metal nitrates. The obtained aerogels were analyzed by BET method, determining the specific surface area (S_{BET}). Photocatalytic behavior of the obtained aerogels was tested by the decomposition of salicylic acid, under UV light. The photocatalytic activity of doped aerogels was compared with the undoped one and with the reference Degussa P25 TiO_2.

Keywords: Ce doped TiO_2, Cu doped TiO_2, Fe doped TiO_2, salicylic acid, photodegradation

INTRODUCTION

The concern for the environmental pollution made the society to reconsider the old path and to create new technologies, less expensive and less polluting.

In the last years the interest for using TiO_2 as a catalyst in photodegradation of organic compounds became wildly spread. It is a stable, non toxic material and is a 3.2 eV band gap semiconductor with attractive photoabsorbtion properties [1]. Under UV light, with wavelength shorter than 380 nm, the electrons from the valence band are excited and jump in the conduction band. The electron–hole pairs thus generated serve as the oxidizing and reducing agents. The photodegradation of pollutants in water takes place due to the OH• radicals, which are formed either through the interaction of water molecules with a hole or through the interaction of oxygen molecules with a hot electron, and which are the key active species [2]. Doping TiO_2 with transition metals (Me) was thought to increase the absorption of TiO_2 to the visible light of solar spectrum [3] and especially to inhibit the recombination of the electron-hole pair photogenerated [3-5] and thus, to increase the photocatalytic activity of TiO_2. Some authors agree the increasing of photocatalytic activity by doping TiO_2 with transition metals [5] while others deny it [6]. Many authors confirmed that the best dopping results are obtained for a concentration of 0.5-1at% metal dopant [4, 5]. Nevertheless the efficiency

* Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania

of TiO_2 photoactivity is depending on many factors such as: the chosen metal dopant, crystallinity, particles size, specific surface area, surface OH groups of TiO_2, time of recombination between the electron-hole pair etc [7].

This aim of this paper is to present the preparation of 1at% cerium, 1at% copper and 1at% iron doped TiO_2 photocatalyst and some photocatalytic results obtained in degradation of salycilic acid.

EXPERIMENTAL

Sample preparation

Iron, copper and cerium doped and undoped TiO_2 were prepared by sol-gel method in acid catalysis, followed by supercritical drying with liquid CO_2. The acid catalyzed sol-gel process was carried out under normal conditions. Two different solutions were prepared: the first one contained 5 ml tetra-iso-propyl ortotitanate - TIP (Merck; >98%) in 10 ml ethanol and the second one 0.049M Fe $(NO_3)_3 \cdot 9H_2O$ (Aldrich) or 0.098M $Ce(NO_3)_2 \cdot 6H_2O$ (Aldrich), or 0.052M $Cu(NO_3)_2 \cdot 3H_2O$ (Aldrich) dissolved in ethanol, doubly distilled water, nitric acid and 10 ml ethanol. After homogenizing, the first solution was quickly added to the second one under vigorous stirring. The corresponding molar ratios of $Me(NO_3)_3$/TIP are presented in Table 1. The $EtOH/H_2O$ and H_2O/HNO_3 molar ratios were 4.89 and 31.59, respectively. The resulting gels were covered and allowed to age for several weeks at room temperature. The solvent was then removed by low-temperature supercritical drying with liquid CO_2, using homemade equipment. The aerogels obtained in this way were calcined at 773 K for 2h in air, using a CARBOLITE furnace, and subsequently characterized.

Sample characterization

The BET surface areas (S_{BET}) were derived from krypton physisorption measurements at 77 K using a home-made installation. Prior to measurements, the samples were degassed to 0.001 Pa at 448 K. S_{BET} was calculated in the relative pressure range of 0.05-0.3, assuming a cross-sectional area of 0.195 nm^2 for the krypton molecule.

Photocatalytic activity

The photocatalytic activity of the doped and undoped TiO_2 aerogels was determined by observing the photodegradation of the salicylic acid. Photodecomposition experiments were performed in a Teflon cell with a quartz window for UV illumination using a 250 W high pressure Hg lamp. The photodegradation profile was obtained by observing the concentration of salicylic acid, measured with a Jasco V-530 spectrophotometer. The cell was kept for 15 min in the dark before the degradation experiment and spectra measurements. The absorbance of the aliquots, withdrawn at every 30 min of the irradiation time, was recorded at 295 nm.

RESULTS AND DISSCUTIONS

Table 1 lists the specific surface area (S_{BET}) of different transition metal doped TiO_2 aerogels, calcined at 2h at 773 K. The biggest specific surface area is obtained for the undoped TiO_2. Cu doped TiO_2 seems to have the biggest S_{BET}, between the transition metal doped TiO_2 aerogels.

Table 1.

Specific surface area (S_{BET}), and apparent rate constant for the transition metal doped and undoped TiO_2 aerogel and TiO_2 Degussa P25, calcined at 773 K for 2h

Me-TiO_2 Sample	**$Me(NO_3)_x$/TIP** (molar ratio)	**S_{BET}** [m^2g^{-1}]	**10^3 x k_{app}** [min^{-1}]
Fe-TiO_2	1.031	65	4.16
Ce-TiO_2	0.575	63	9.75
Cu-TiO_2	0.618	80.5	6.89
Undoped TiO_2	0	131	12.9
P25 Degussa	0	53	2.5

The evolution of the salicylic acid concentration in time for both doped TiO_2 aerogels and TiO_2 Degussa can be closely described by exponential curves (Fig. 1). Thus, an apparent rate constant k_{app} (Tabel 1) derived from the expression:

$$C = C_0 \exp(-k_{app} t) \quad (1)$$

can be determined. This behavior is generally found in the photocatalytic degradation of organic pollutants in water. A Langmuir-Hinschelwood mechanism [7] with the rate proportional to the surface coverage combined with a low initial concentration of the pollutant leads to a pseudo first–order kinetic law [9, 10].

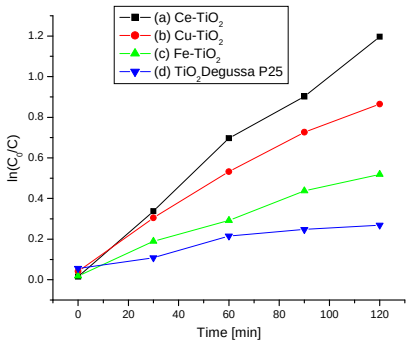

Fig.1. Salicylic acid degradation on different photocatalysts: (a)Ce-TiO_2, (b) Cu-TiO_2, (c) Fe-TiO_2, (d) TiO_2 Degussa P25

It is known that photodegradation is depending on photogenerated OH• radicals. The Ti^{4+}-OH• entity is formed by a hydroxyl group which traps a hole [7]. The goal of doping with transition metal was for increasing the time of recombination between electrons and holes photogenerated. The place of metal ions in the TiO_2 lattice can have different effects. A substitution position of a titanium ion with a metal ion in the TiO_2 lattice is desired in order to reach this goal. In this case metal ion is capable to create traps in the band gape of TiO_2 (Fig.2) and thus, the time of recombination of the electron hole pair is increased. Experimentally was revealed that metal dopants can take different forms in TiO_2 matrix: substitution, interstitial position and/or especially as metal oxides [7, 11].

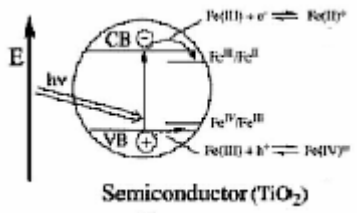

Fig.2. Photocatalytic mechanism of doped TiO_2, in the presence of iron doping ions [4]

All doped samples reveal a lower photocatalytic activity (table 1) comparing with the undoped TiO_2. One possible explanation, as Coronade et al. [12] remarked on Ce doped TiO_2 compared with the undoped one, is that the photogenerated holes are stabilized as Ti^{4+}-O^- radicals due to CeO_2 presence, which might exist in Ce-TiO_2. In addition, the presence of the metal oxide in the transition metal doped TiO_2 can be an impediment not only for OH groups that form on the TiO_2 surface but also for the adsorption sites of TiO_2 destined to the organic pollutants. In doped samples can exist a partial blockage on the surface sites available for organic pollutant.

However, comparing Ce-TiO_2 with the undoped one, can be observed that S_{BET} of Ce-TiO_2 is smaller than the undoped one. This could lead to the conclusion that the k_{app} of photodegradation process of the Ce doped TiO_2 could be only due to its small S_{BET} and not necessary due to CeO_2. In this case Ce ions could be incorporated in the TiO_2 lattice and thus, the increasing time of recombination of the electron – hole pair by Ce dopping could be considered. Ce^{4+} is a scavenger of electrons and the electron trapped in Ce^4/Ce^{3+} is transferred to the surrounding adsorbed O_2, increasing the photocatalytic activity of TiO_2 on organic compunds. The process is described below [13]:

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \quad (2)$$

$$Ce^{3+} + O_2 \rightarrow \bullet\, O_2^- + Ce^{4+} \quad (3)$$

Fe doped TiO_2 has almost the same S_{BET} with Ce doped TiO_2 but its potocatalytic activity is the smallest. This result is in accordance with the literature [3], where Fe doped TiO_2 was found to have low fotocatalytic activity. Cu doped TiO_2 presents the biggest S_{BET}, comparing with the other doped samples but its photocatalytic activity is lower than that of Ce doped TiO_2. However, all obtained TiO_2 aerogels present a better photocatatytic activity comparing with Degussa P25 TiO_2.

Further studies are necessary to clarify the effects of surface area, microstructure, doping, UV-VIS absorbtion, presence of OH groups on TiO_2 surface, crystalline structurure on photocatalytic activity of doped and undoped TiO_2

CONCLUSIONS

1at% Ce, 1at% Cu, 1at% Fe doped and undoped TiO_2 aerogels were prepared by sol-gel method. The photodegradation process of salicylic acid on doped and undoped TiO_2 aerogels shows a better photocatalytic activity for the undoped TiO_2. One possible explanation is the partial blockage created on TiO_2 surface due to the formation of metal oxides during dopping. However, further research has to be done in order to clarify the causes that determined the lower photocatalytic activity of the doped samples comparing with the undoped one. All obtained samples have a better photocatalytic activity comparing with the reference Degussa P25 TiO_2

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