

HYDROTHERMAL SYNTHESIS OF HYBRID TiO₂-CARBON MATERIALS FOR APPLICATION IN PHOTOCATALYSIS

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Introduction

Materials based on TiO₂ are interesting photocatalysts for the elimination of pollutants such as volatile organic compounds¹. There is a growing interest in developing more efficient materials using simple and environmentally friendly synthesis methods. By incorporation of carbon to titania, the photocatalyst can enhance its electrical conductivity, stabilize the anatase phase (increasing the temperature required for its transformation to rutile), improve its crystallinity and favour the adsorption of organic compounds, among other positive aspects². Therefore, the objective of this work is to prepare TiO₂-carbon photocatalysts through a simple and inexpensive hydrothermal process in which saccharose is used as an economic carbon precursor. The novelty of this work is based on the simplicity of the synthesis procedure that occurs in one step, at low temperature, and avoiding the use of surfactants. The concentration of HCl solution used as hydrolysis medium has been selected as the synthesis variable. The properties of the TiO₂-C catalysts have been compared with those of analogous pure TiO₂ catalysts prepared by the same method in a previous work³.

Materials and Methods

In a typical synthesis, 1.25 g of saccharose were dispersed in ethanol (20 ml), TTIP was added (4 ml), and after stirring (room temperature, 1h) and treatment in ultrasounds bath (30 min), a solution of HCl (4 ml) of variable concentration (0.5, 0.8, 1, 5 or 12 M) and ethanol (10 ml) was added dropwise. After stirring (1h) the mixture was transferred to a 50 ml Teflon-lined stainless-steel autoclave, submitted to heat treatment (180 °C, 12 h), and afterwards cooled down to room temperature. Then, the solid was filtered, dried (100 °C, 12 h) and, finally, submitted to a post-synthesis heat treatment in air in a muffle (5 °C/min up to 350 °C, 2 h). The materials were named as TiO₂-C-XM, where X refers to the molar concentration of the HCl solution used ([HCl]). The photocatalysts were characterized by N₂ adsorption, XRD and TG and tested in the photocatalytic oxidation of propene (0.11 g of photocatalyst, 100 ppmv propene in air (30 or 60 ml/min), room temperature, UV lamp of maximum λ at 365 nm). The outlet gases were analyzed by mass spectrometry (Balzers, Thermostar). TiO₂-P25 (Evonik) was used as reference.

Results and Discussion

Table 1 presents the characterization results of the TiO₂-C and TiO₂ materials. It is remarkable that after the post-synthesis heat treatment the carbon content strongly decreases, ranging between 0.34 and 0.39 wt % (in comparison to 30 wt.% carbon previously present). In general, the textural properties of TiO₂-C and TiO₂ materials are quite similar. However, the presence of carbon during the synthesis strongly influences the development of TiO₂ crystalline phases: TiO₂-C photocatalysts contain only anatase (probably because carbon dissipates heat during the heat treatment), while analogous pure titania samples contain mixed crystalline phases (anatase-brookite or anatase-brookite-rutile), in a proportion depending on the HCl concentration³. The anatase content is higher in TiO₂-C than in TiO₂ catalysts. The materials have larger surface area and porosity, smaller crystal size and

higher amorphous phase contribution than P25. In general, when increasing the HCl concentration, the textural properties get poorer and the crystal size increases.

Table 1. Characterization of the TiO₂-C and TiO₂ photocatalysts (P25 as reference material).

Samples	S _{BET} (m ² /g)	V _T (cm ³ /g)	Crystalline TiO ₂ (%) A-B-R*	Average anatase size (nm)	Amorphous TiO ₂ (%)	wt. % C**
TiO ₂ -C-0.5M	137	0.23	73-0-0	8	27	0.34
TiO ₂ -0.5M	135	0.26	69-11-0	8	20	--
TiO ₂ -C-0.8M	131	0.22	70-0-0	9	30	0.35
TiO ₂ -0.8M	134	0.36	60-16-1	8	23	--
TiO ₂ -C-1M	103	0.19	78-0-0	9	22	0.39
TiO ₂ -1M	116	0.33	62-17-2	9	19	--
TiO ₂ -C-5M	93	0.15	79-0-0	9	21	0.38
TiO ₂ -5M	100	0.26	50-23-6	10	21	--
TiO ₂ -C-12M	109	0.17	75-0-0	10	25	0.35
TiO ₂ -12M	110	0.32	66-9-0	11	25	--
P25	55	0.18	73-0-14	22	13	--

*A= Anatase, B= Brookite, R= Rutile. ** Carbon content after post-synthesis heat treatment at 350 °C.

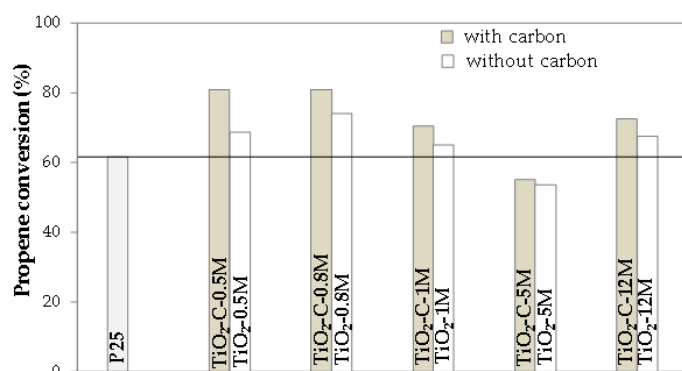


Figure 1. Propene conversion (at 30 ml/min) in TiO₂-C, TiO₂ and P25 samples.

Regarding conversion (Fig. 1), TiO₂-C materials are more active than analogous pure TiO₂ ones (propene conversions about 10% higher for TiO₂-C samples). The higher activity could be related either with the carbon present, despite its low amount, or with particular TiO₂ properties developed during the synthesis because of the presence of carbon. The activity of TiO₂-C materials is linked to their textural properties, and a good correlation of propene conversion with BET surface area (S_{BET}) has been found.

Conclusions

TiO₂-C photocatalysts have been prepared by a simple, one step, hydrothermal synthesis in mild conditions. The textural properties of the TiO₂-C samples are similar to those of analogous pure TiO₂ samples, but they contain only anatase instead of mixed phases, and their anatase content is higher. The TiO₂-C photocatalysts are more active for propene oxidation than the corresponding TiO₂ samples and also more active than commercial TiO₂-P25.

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