PREPARATION OF NOVEL X% Li/TiO$_2$ (x = 1%, 2% and 4%) AND THEIR ACTIVITIES UNDER VISIBLE LIGHT

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Series of metal doped titanium dioxide were synthesized with the aim to enhance the photocatalytic activity under visible irradiation. x% Li doped TiO$_2$ catalysts (x = 1%, 2% and 4%) were prepared using hydrothermal method. The samples were characterised by specific surface area S$_{BET}$, X-ray diffraction XRD, diffuse reflectance spectroscopy DRS and photocatalytic activity.We succeeded to obtain high specific surface area samples. In fact, it increases to reach an optimum at 2% dopant amount. XRD analysis showed that all samples are single Anatse phase whatever dopant amount level. The photocatalytic activity was tested in methylene blue degradation under visible irradiation. Two different power lamps were used in order to investigate effect of irradiation condition. These new photocatalysts exhibited visible light activity similar to PC500 to degradated MB. The results were discussed in terms of donor electron level creation in the band gap.

1. Introduction

Main nature issues are caused by polluants propagation in the atmosphere or seeping into the soil. Sources of aquatic contamination are concentrated in the textile industries discharge (dyes), human waste and pharmaceuticals discard (phenolic compounds). Faced with these dangers, modern society engaged a public priority with the aim of purification and protection of the human environment. Currently, scientific researches are focused in the finding of effective means for pollution control through various economic and efficient processes. Thus, photocatalysis has proved an interesting path for the purification of contaminated water. This process uses energy photonics to catalyze chemical reactions. Its applications include the decomposition of water into hydrogen and oxygen [1] and mineralization of organic contaminants in the aquatic environment [2].

In recent years, catalysts such as TiO$_2$, ZnO, WO$_3$, SnO$_2$ [3-5], ZrO$_2$ [6], Nb$_2$O$_5$, ZnS and CdS [7] were used as organic contaminants oxidation photocatalysts. Among these materials, TiO2 proved to be an excellent catalyst [6, 8-11]. It has a good chemical stability, in addition to its low cost [12]. However, his band gap energy (3.0eV for the anatase variety and 3.2eV for rutile variety) means that only 5% of the solar spectrum can be used [3, 6, 7, 12]. Furthermore, quick electron-hole recombination is a limiting factor of the catalyst effectiveness [8,13]. Thus doping by cations of different valence of titanium in the TiO$_2$ can have a double effect: Reduction of the energy gap, which has the effect of moving the absorption into visible region and Reduction in the electron-hole recombination.

Recent work relating to the doping of TiO$_2$ by metal [14], transition metals [8, 10, 11] and rare earth and lanthanide [17-20] showed that doping can increase the photoactivity even with small loading amount. The results continue to be the subject of much discussion. In our investigation, we aim to obtain powerful doped TiO$_2$ catalysts owing small gap value and high surface area. We succeeded to obtain fifty doped catalysts (Ce, Li, Co, Mn, Mg, La, Ga and Cu) with important SBET (regarding P25) at small doping content. In this paper, we focus on Lithium doped titanium dioxide catalysts prepared through hydrothermal route. Herein we try to investigate parameters affecting photoactivity such as doping amount, crystallinity and specific surface area.

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2. Experimental

2.1. Preparation of the samples

All reagents were obtained from ACROS and used without further purification. The experimental procedure for the preparation of x% Li/TiO$_2$ catalysts is described in detail in the following. Tetrabutyltitanate was dissolved with acetic acid. In another container, an amount of lithium precursor was dissolved with ethanol and then added to tetrabutyltitanate solution. The resulting mixture was transferred into autoclave cell which was hanged either at 60°C for 7 days or 120°C for 4 days. After filtration and drying at 80°C for 24 hours, the powder was calcinated at 450°C for 12h.

2.2. Characterization

Crystalline phase in the sample were identified from X ray powder diffraction (XRD) measured by using PANalytical diffractometer with CuKα radiation. Total specific surface area (S$_{BET}$) of Li doped TiO$_2$ catalysts were measured from N$_2$ adsorption at 77 K using a Micrometrics ASAP 2010 analyser. The diffuse reflectance spectra (DRS) of the samples were recorded with a Shimadzu UV 3101 PC spectrophotometer. Scanning range of the DRS spectra was 190-800nm. The photocatalytic activities of these catalysts were tested in MB degradation. The experiment was carried out using two different reactors. The first reactor consists on Teflon tube cooling system which was introduced in silicone oil container on which was put a 400 mL baker that contain the reacting solution. The system was irradiated with a 100 watt visible light lamp tacked at well defined distance. The second reactor is small scale system consisted of a glass reactor (350 mL). A 60 watt lamp was placed in a glass tube which was immersed into the photoreactor. In this latter were filled 120mL of MB solution of 30 mg/L to which was added 60 mg of catalyst. This system is equipped by a circulating water jacket to cool the reacting solution. Prior to the photoxidation, the solution was stirred for one hour in the dark.

3. Results and discussion

3.1. Analysis of X-ray diffraction patterns

The XRD patterns of Li doped TiO$_2$ samples are shown in Fig.1. All diffraction peaks can be assigned to the anatase phase without any indication of other crystalline by products. The X-ray diffraction patterns of which were indexed based on tetragonal lattice according to JCPDS data cards. When examining these patterns, it is worthy to note the widening of the peaks when increasing dopant amount. There must be an optimal dopant amount since, as it can be seen, 2% Li/TiO$_2$ sample labelled Sa 7 shows the widest peaks. This can be explained by reducing in grain sizes that lead necessarily to high specific surface area. We have used DebbeySherrer equation to calculate the average grain size. As estimated, increasing dopant amount is accompanied with reducing in grain size. And the smallest one are recorded at 2% level amount (Table 1).
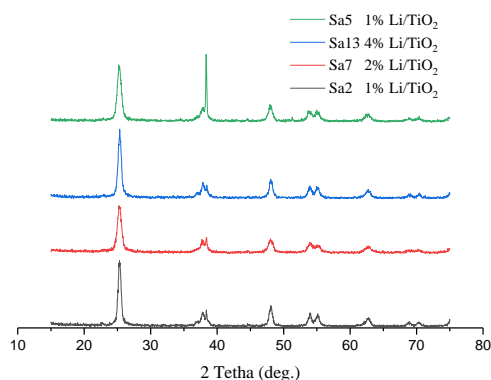

Fig.1.X-ray diffraction pattern of x%Li-TiO$_2$ (x = 1, 2 and 4%).

In fact, Wang et al [21] suggest that the presence of dopant favours sintering process. This idea was maintained by Hamal et al [22] who showed that sintering of small particles into the bigger particles was more pronounced for the "undoped" catalysts. In fact, results of electron micrographs (not shown here) indicate that increasing loading level make the powders made from smallest particles (particles size vary from 23nm to 10nm, these value are close to that estimated from Debbeye Sherrer equation).

$$D = \frac{0.9\lambda}{\cos\theta\sqrt{(\Delta_m^2(2\theta) - \Delta_i^2(2\theta))}} \tag{1}$$

Table1 reports value of specific surface area of x% Li/TiO$_2$ (x = 1, 2 and 4%). Whatever doping amount, surface area was about hundred square meters per gram. A noticeable result is observed, the greater surface were recorded at 2% dopant amount. This is close to that estimated from X-ray diffraction. Again, Bellardita et al [23] showed that there is usually an optimum of dopant content at which measured surface area is the highest (e.g S_{BET} (0.1% Eu/TiO$_2$) = 120m²/g and S_{BET} (0.5% Eu/TiO$_2$) = 130m²/g and S_{BET} (1% Eu/TiO$_2$) = 124m²/g).

Table 1. Specific surface area, grain size and band gap values of x%Li-TiO$_2$ (x = 1, 2 and 4%).

Sample	Symbol	S_{BET} (m²/g)	d (nm)	Eg (eV)
TiO$_2$	PC500	350		3.24
1% Li/TiO$_2$	Sa 5	92.51	18	3.17
	Sa 2	108.00	11	3.10
2% Li/TiO$_2$	Sa 7	134.65	10	3.08
4% Li/TiO$_2$	Sa 13	100.30	13	3.00

3.2. Optical study and analysis of UV–Vis diffuse reflectance spectra

Optical characterization is a significant tool, which is used to assess band gaps and quantum confinement effects. The DRS spectra were determined at 200–700 nm to study the effect of carbon doping on the band gap. The DRS spectra of the reference PC500 and Li doped TiO$_2$ nanoparticles are shown in Fig. 2. A strong absorption edge appears between 340 and 370 nm for all the samples. It was found that increasing concentration of lithium doping, leads to the shifting of the absorption band toward the high wavelength region. The absorption edge of the Lithium doped TiO$_2$ nanoparticles red shifts at high wavelength regions compared with that of the PC500 TiO$_2$ nanoparticles. The shifts in the absorption edge can be due to the influence of quantum confinement.
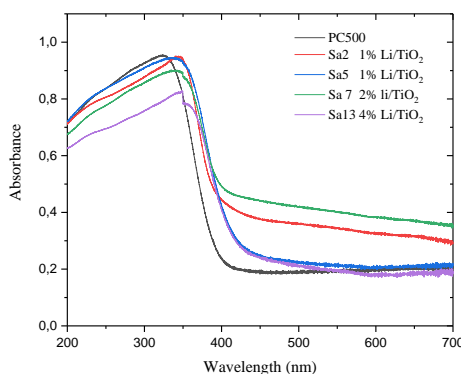

Fig. 2. DRS spectra of PC500 and x%Li/TiO$_2$TiO$_2$(x = 1, 2 and 4%) nanoparticles samples.

The band gap energies of the TiO_2PC500 and Lithium doped TiO_2 nanoparticles were estimated from the DRS spectra by using the Kubelka–Munk function $(F(R)^2$ versus energy, in electron volts). The linear portion of the curve was then extrapolated to $F(R)^2 = 0$ (Fig. 3). The optical absorption factor (α) is calculated with $F(R) = \alpha = (1 - R)^2 /2R$, where R is the reflected light percentage. The optical band gap energy (Eg) and incident photon energy (hv) correspond to the transformed Kubelka– Munk function, namely, $[F(R) h\nu]^n = A(h\nu - Eg)$, where A is a constant related to transition probability, Eg is the band gap energy, and n is the power index of optical absorption[20,24,25]. The value of n is equal to 2 or 1/2 for direct or indirect allowed transition, respectively. The band gaps of the samples, which decrease with increasing lithium concentration, are listed the table 1. This consistent result let us suppose that the presence of dopant seems to favour electron donor level creation in the band gap of the host semiconductor. Otherwise it enhances its visible light response.
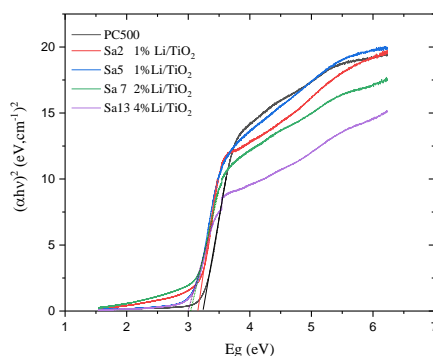

Fig. 3. Graphical representation of absorbance and F(R) spectra without considering electronictransitions: F(R) versus Eg , for catalysts x%Li-TiO$_2$ (x = 1, 2 and 4%) and PC500.

3.3. Visible photocatalytic activities of prepared catalysts

We studied the degradation of methylene blue MB as a model reaction to investigate the photocatalytic activity of doped titanium dioxide catalysts and the degradation mechanism on these catalysts under visible light irradiation. Table 2 listed the results recorded under 100 and 60 Watt irradiation. As expected in the first case, apparent first order rate constant was enhanced with Li doped TiO_2 whatever doping amount with respect to PC 500. However under 60 Watt irradiation, this former presents faster degradation rate although x%Li/TiO_2 constant rates are hanging to a similar behaviour as can be seen in the Fig.4. Apparently, 2%Li/TiO_2 labelled Sa7 possess the greatest photoactivity under both irradiations. It is worthy to note that this catalyst had a much superior surface area to Sa5 and Sa13. In contrary, if we admit that surface is the main factor affecting rate constant (Fig.5), we have to reply to the question addressed to PC 500; which photoactivity is the lowest in spite of its highest specific surface area. Herein surface effect becomes not easily explainable. It seems to be more reasonable to report rate constant per gram. This provides thus a potential advantage.
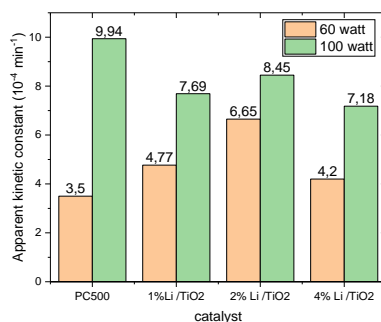

Fig. 4.Kinetic profiles of catalysts in the MB photocatalytic degradation under visible light.
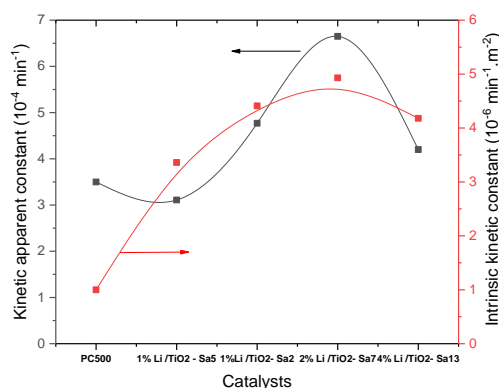
Fig. 5.Evolution of apparent and intrinsic kinetic constants for different catalysts in the MB photocatalytic degradation under visible light.

As depicted in Table 2under 100 watt irradiation, whatever dopant amount, the as prepared catalysts show the same response. At the naked eye, we can roughly say that we have succeeded to obtain new Li/TiO_2 catalysts weakly doped with much more effective visible light response regarding to PC 500 which is known as one of the best photocatalysts in the presence of visible irradiation.

Table 2. Constant rate of x%Li-TiO$_2$ (x = 1, 2 and 4%) recorded under 60 and 100 watt irradiation in MB degradation.

Sample	Symbol	Apparent kinetic constant (k_{app}) $(10^{-4}min^{-1})$	S_{BET} (m^2/g)	Intrinsic apparent kinetic constant $k^*_{app}(10^{-6}min^{-1}.m^{-2})$
100 Watt visible irradiation				
TiO$_2$	*PC 500*	3.50	350	1.00
1% Li/TiO$_2$	*Sa 5*	3.11	92.51	3.36
	Sa 2	4.77	108.00	4.41
2% Li/TiO$_2$	*Sa 7*	6.65	134.65	4.93
4% Li/TiO$_2$	*Sa 13*	4.20	100.30	4.18
60 Watt visible irradiation				
TiO$_2$	*PC 500*	9.94	350	2.84
1% Li/TiO$_2$	*Sa 5*	7.69	92.51	8.31
2% Li/TiO$_2$	*Sa 7*	8.45	134.65	6.27
4% Li/TiO$_2$	*Sa 13*	7.18	100.30	7.15

Additionally, we could noted out that rate constant is mainly sensitive to surface effect but there is no more parallelism when either compared to PC 500 or deeply focusing on value recorded under 60 watt irradiation. The remarkably result that we have to shed light on is that the as synthesized catalyst were found to have better photoactivity per gram. Thus there are other parameters that we have to take into account such as electron hole scavenging. Therefore the electronic properties of the catalyst are vital for their catalytic activity. When the catalyst is illuminated with radiation whose energy is greater than or equal to the energy gap, electrons are excited in the valence band into the conduction band. Electron diffuse is then much more facilitated for the as prepared catalysts because of band gap narrowing. So that, for the same wavelength irradiation, Li doped catalysts are able to generate more electron-hole pair than PC500.

This induces the faster MB decomposition recorded in Table 2. Reaction rate enhancement can also be due to dopage with lower valence ion than titanium. Thereby, a charge imbalance could be created and then MB could be strongly absorbed and oxidized.

4. Conclusions

We succeeded to prepare new series of Li doped titanium dioxide by varying dopant amount (x = 1, 2 and 4%). All the samples are well crystallized anatase phase. The specific surfaces areas of these catalysts range between 92 and 134 m²/g. An optimum was observed at 2% loading level. Photoactivity was carried out in the degradation of methylene blue.

We succeeded to improve visible response of doped titanium dioxide regarding PC 500. Herein, we shed light on importance of catalyst contact surface with the pollutant molecule. Taking into consideration that efficiency of all the catalysts depends on electron-hole generation. Other analyses have to be done such as XPS and FTIR in order to well explain our investigation.

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