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Incorporation of Lithium into TiO_2 Host and its Application in Photocatalysis

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In this work we prepared the stable photocatalyst by the incorporation of lithium into TiO_2 host. Lithium hydroxide was used as the modifier. Titanium host material was in two forms: commercial titanium dioxide (anatase, Police Chemical Factory, Poland) and titanium slurry that was slightly crystallized. The prepared materials have been characterized by XRD, FTIR and UV-Vis/DR methods. The XRD analysis showed that the main component of these samples was lithium titanate – Li_2TiO_3. The photocatalytic activity of prepared materials was tested in the photocatalytic reactions of oil and phenol decomposition in water. It was found that both oil and phenol undergo the photocatalytic decomposition over lithium-TiO_2 and the activity of these materials was higher in comparison with that of pure anatase host.

Keywords: modification of TiO_2 host; photocatalysis; water purification

INTRODUCTION

It is well established that n-type semiconductors, like TiO_2, in aqueous solution under light illumination with energy higher than the bandgap of the semiconductor, induce the catalytic decomposition and often the complete

mineralization of organic compounds [1-3]. TiO_2 in the photocatalytic processes may be used pure or modified, which can enhance its activity [4,5].

In this work we modified the titanium dioxide host with lithium and applied this material in the reaction of decomposition of oil and phenol in water. These two organic compounds were chosen as the representatives of the most dangerous pollutants for water environment.

EXPERIMENTAL

Preparation of photocatalyst

Titanium dioxide was modified by the incorporation of lithium into TiO_2 host. As modifier lithium hydroxide was used. Titanium host material was in the two forms: (1) commercial titanium dioxide (anatase, Police Chemical Factory, Poland) and (2) non-calcinated titanium slurry produced by Police Chemical Factory which was slightly crystallized.

A photocatalyst sample based on anatase was prepared by the impregnation method in aqueous solution of lithium hydroxide (4g of lithium per 20g of anatase) and drying followed by the calcination at temperature of 550°C for 12 hours. After calcination the sample was powdered and than washed with distilled water until the neutral reaction in the filtrate was reached.

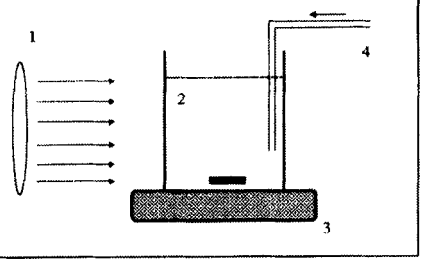
The photocatalyst sample based on non-calcinated titanium slurry was prepared by mixing of 4g of lithium and 20g of titanium slurry. The obtained material was than treated as described above for the anatase sample.

Experimental conditions

The photocatalytic reactions of phenol and oil decomposition in water were carried out at atmospheric pressure using air as the oxidant in the Pyrex batch photoreactor (Figure 1). The photocatalyst was suspended in 500 cm^3 of contaminated water by magnetic stirring. The UV light source was the VT-400 (Poland) mercury lamp with power of 370W and the light intensity of 49W m^{-2}. The reaction mixture was aerated (air flow rate: ca. 0.1 dm^3 min^{-1}). The simplified diagram of the apparatus is shown in Figure 1. After each reaction,

the catalyst was separated from the solution, and the reaction mixture was analyzed by the IR method using SPECORD M80 (Germany) spectrometer, in the case of the oil decomposition reactions and by UV/VIS method using SPECORD M40 (Germany) spectrometer in the case of phenol.

Figure 1. Scheme of apparatus for photocatalytic decomposition of oil and phenol. 1-light source, 2-batch photoreactor, 3-magnetic stirrer, 4-air inlet.



The experiments for oil and phenol decomposition were carried out under the following conditions: without the photocatalyst and under UV illumination, without illumination and in the presence of the photocatalyst, under illumination and with the presence of the photocatalyst. The oil and phenol decomposition was not observed for the reactions carried out without photocatalyst or in the dark, while in the reactions with UV illumination and in the presence of photocatalyst the oil and phenol decomposition was observed.

RESULTS

The prepared materials appeared to be active in the reactions of phenol and oil decomposition in water, however the activity of photocatalyst prepared from anatase was higher. The results of the activity tests of the samples are presented in Figure 2 (Li/A-lithium/anatase, Li/S-lithium/slurry). The reaction time was

Figure 2. Activity test of lithium photocatalysts

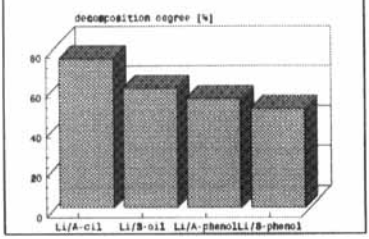
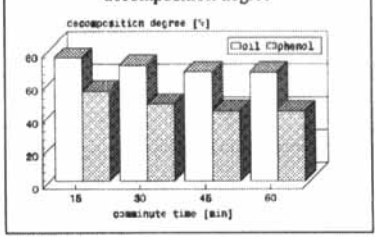


Figure 3. Effect of the particle size on decomposition degree

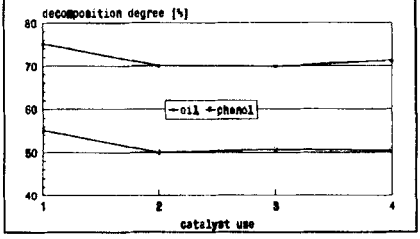


1.5 h and the catalyst content was 0.4 g dm^{-3}. The complete oil decomposition was achieved after 2 h illumination, while the complete decomposition of phenol in water was achieved after 2.5h of illumination with the same catalyst content. Decomposition degrees of phenol and oil (the same reaction conditions) using pure titanium dioxide were 42% and 68%, respectively.

It is known that the photocatalyst content affects the photocatalytic reactions. The obtained results show that the optimal content of Li/A catalyst amounts to 0.3 – 0.7g dm^{-3} for oil and 0.2 – 0.5g dm^{-3} for phenol.

We have found that the degree of grinding influences the degree of decomposition of oil and phenol in water. The higher is the degree of fineness the lower is decomposition degree (figure 3). These experiments were carried out with the Li/A catalyst (0.4 g dm^{-3}).

Figure 4. Lifetime of Li-TiO_2



In order to examine the stability of catalytic activity (lifetime), the experiments with used photocatalyst were performed. The obtained results showed a slight decline in activity after the first reuse. In the subsequent uses the activity remains stable. The results of these experiments are shown in figure 4.

Figure 5 shows the diffractogram of photocatalyst precursors, e.g. commercial titanium dioxide (anatase) and slightly crystallized titanium dioxide. It can be seen from Figure 5a that the commercial titanium dioxide

Figure 5. Diffractogram of a) anatase and b) TiO_2 slurry

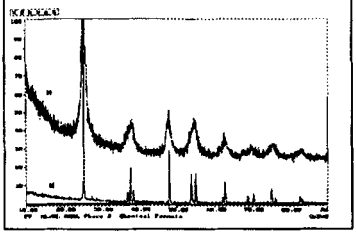
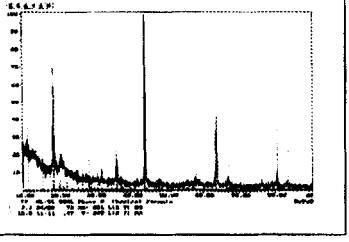
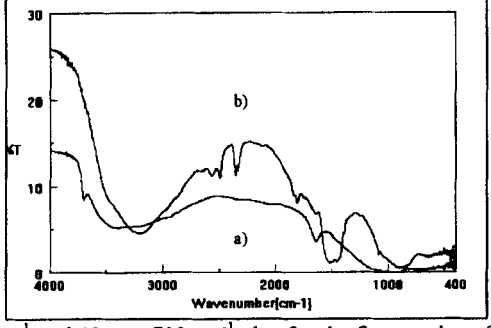


Figure 6. Diffractogram of Li-TiO_2



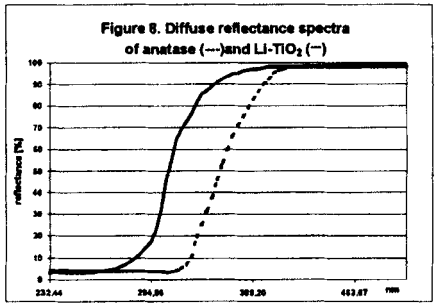
contains only one, clear anatase phase (JCPDS card No 21-1272) being very well crystallized. Figure 5b present the diffractogram of amorphous titanium precursor. The peaks are very broad which indicate for a weak crystallinity of this material. Diffractogram of anatase modified with lithium is presented in Figure 6. The main component of this sample is lithium titanate – Li_2TiO_3 (JCPDS card No 8-249 and 33-831). Li_2TiO_3 has a cubic structure with a = 4.1355 ± 0.0007Å [6]. The sample prepared from titanium slurry (not presented here) contains various lithium titanates which were not so well crystallized. TiO_2 modified with lithium is more active than pure TiO_2, therefore it can be stated, that well crystallized lithium titanate which was formed during modification is responsible for the activity enhancement.

Figure 7. FTIR spectra of a) TiO_2 and b) Li-TiO_2



FTIR analysis also confirmed changes in the TiO_2 structure (Figure 7). The new absorption bands appeared in the range of 2700 – 2250 cm^{-1} and broad bands in the ranges of 1600 – 1300 cm^{-1} and 1250 – 700 cm^{-1} also for the frequencies of 1835 and 1800 cm^{-1}. The spectrum of anatase shows the absorption band by 3695 cm^{-1}. This peak disappears on the spectrum of Li-TiO_2.

The photocatalyst samples were also analysed by UV-Vis method using SPECORD M40 spectrometer equipped with an integrating sphere accessory for diffuse reflectance. $BaSO_4$ was used as a reference. Spectra of Li-TiO_2



and anatase are shown in Figure 8. Li-TiO_2 shows a shift in the band edge, thus the band gap energy of this material which equals 3.9 eV is 0.7 eV higher than for anatase (3.2 eV).

CONCLUSIONS

The modification of titanium dioxide host, both commercial and titanium slurry, with lithium hydroxide results in the stable material, which is active in the reaction of decomposition of organic compounds in water under UV illumination. The activity order of the photocatalytic materials is as follows: titanium slurry<anatase<Li/S<Li/A. The band gap energy is shifted up to 3.9 eV after modification and the creation of new bands in IR spectra were observed. The complete decomposition of phenol in water was achieved after 2.5 h of illumination with catalyst content of 0.5 g. The complete oil decomposition was achieved after 3.0 h of illumination with the same catalyst content. The catalytic activity decreases slightly after the first reuse, however it remains stable in the subsequent uses. The degree of decomposition of oil and phenol in water is effected by the particle size of the photocatalyst. For the same amount of photocatalyst, the smaller are the particles the lower is decomposition degree. The main component of the modified photocatalyst is lithium titanate – Li_2TiO_3, which is probably responsible for the enhancement of activity. The resulting modified TiO_2 could be a good host material for further intercalation.

References

[1] M. Schiavello -editor: Photocatalysis and Environment, Kluwer, Dordrecht (1988).
[2] D. F. Ollis and H. Al-Ekabi, *In Proceedings of 1st International Congress on Photocatalysis,* Elsevier Science Ltd (1993).
[3] D. M. Blake, *NREL/TP-430–22197,* Golden Co (1997).
[4] T. Sasaki. S. Nakano, S. Yamauchi and M. Watanabe, *Chem. Mater.* **9**, 602 (1997).
[5] W. Choi, A. Termin and M.R. Hoffmann, *J. Phys. Chem.* **98,** 13669 (1994).
[6] Gmelins handbuch der anorganischen chemie (8 auflage), system number 41, Verlag Chemie, GMBH., Weinheim/Bergstrasse, 383 (1951).