Leucoxene photocatalysts for water purification

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Abstract. The study of photo catalytic efficiency of leucoxene (Pizhemske deposit, Russia) and synthesized on its base rutile and rutile modified with Pt was made. The degradation of trichlorphenol (TCP) under UV irradiation was used as a test reaction. The results showed that specific surface area of leucoxene and as-synthesized rutile is extremely low what predetermines the low photocatalytic activity of these samples. Nevertheless, trichlorphenol could be effectively oxidized under UV light when the Pt modified rutile crashed to 13 nm particle size is used as a photocatalyst.

1. Introduction
Photocatalysis using semiconductor particles for effective water purification from organic compounds and viruses has received growing attention since 1970s [1]. Among semiconductor materials (generally metal oxides: ZnO, TiO$_2$, Fe$_2$O$_3$, CdO, etc) titanium dioxide has been accepted as one of the most promising photocatalysts due to it high photosensitivity, good stability and non toxicity [2, 3]. However, the UV irradiation is needed for the activation of catalyst because of the 3.0 eV band gap for rutile and 3.2 eV for anatase. Other physical properties, mainly crystals phase, also influence the efficiency of organic photodegradation over TiO$_2$: thus, anatase is considered to be much more photoactive than rutile [4]. Nevertheless, the activity rutile can be enhanced by several methods, such as doping of transition or noble metal ions [5] or preparing hybrid semiconductors [6]. Namely, the efficiency is higher if Pt particles dope rutile and could contact simultaneously with organic pollutant to be decomposed. This leads to an effective transfer of electrons trapped on the metal to perform the reduction reaction with O$_2$, whereas the holes could participate in the oxidation reaction to their best abilities [7].

In comparison with commercially available titanium dioxide natural rutile is cheaper and easier to be obtained and can be used as cost-effective photocatalyst. It can contain a number of impurities which can affect its activity. In this study we used natural rutile obtained from Pizhemske deposit (Russia) as a catalyst for 2, 4, 6-trichlorphenol (2, 4, 6-TCP) photodegradation. Titaniferous sandstones of the Pizhemske deposit compose a malorucheysk suite, which is locally spreaded (6x18 km) in the North of the Vymsk-Volsk ridge (Middle Timan, north-east part of Europe). This suite forms the Pizhemske sag. A mineral content of the ore is prevalently formed by leucoxene which is believed to have replaced the ilmenite [8, 9]. Rutile was obtained from leucoxene concentrate using strong alkali solution. Pt doping was used to enhance its photoactivity.

2. Experimental

2.1. Preparation of rutile from leucoxene concentrate
Leucoxene concentrate was obtained from heavy sands of Pigemskoe deposit (Russia) and was treated to remove quartz and minor impurities using the following method. Leucoxene concentrate was mixed with 10 M NaOH solution under vigorous stirring. The obtained mixture was kept in Teflon autoclave at 130 °C for 72 h. After cooling at room temperature the brown precipitate was washed with distilled water and centrifuged for several times until the pH 7.

2.2. Preparation of Pt doped rutile
The tetraammineplatinum(II) hydroxide hydrate (Pt(NH$_3$)$_4$(OH)$_2$H$_2$O, mol weight: 297.21 g/mol) was used in such an amount that the sample would contain 1 % of Pt. The 7 mg Pt complex was added to 450 mg of rutile sample. First the platinum salt was dissolved in 2 ml of distilled water than the sample was put in this solution and stirred for 3 hours. The obtained mixture was dried in a water bath at 90 °C. The salt was decomposed by a programmed heat treatment in two steps: I. 2 °C/min, 150 °C, 0,5h, II. 4 °C/min, 480 °C, 4h. Than it was reduced in the TPR apparatus in H$_2$/Ar gas flow at 350°C for 1h.

2.3. Photocatalytic measurements
A batch type cylindrical photochemical quartz reactor with the volume of 350 cm$^3$ was used, having a UV tube, cooled by circulating water, along the axis of the reactor cylinder. The oxidative degradation of 2,4,6-TCP in water was studied while the water-catalyst suspension was stirred with a magnetic stirrer, irradiated by a 150-Watt UV lamp (TQ 150 Z2). The starting concentration of 2,4,6-TCP was 0.375 mmol/l. The catalyst concentration was 1 g/l. At certain time intervals 2 cm$^3$ aliquote was taken from the reactor and analyzed by ion chromatography using Varian Diode Array HPLC apparatus, Hypersil C18 inverse phase column, and 60-40 % acetonitrile-water mobile phase.

3. Results and discussion
According to XRD patterns (Fig. 1) leucoxene concentrate consists of two main mineral phases: rutile and quartz. Using semi-quantitative analysis of XRD pattern the 3:1 quartz to rutile ratio was determined. The processing of leucoxene concentrate with strong NaOH solution removes quartz completely. Peaks corresponding for the Pt particles impregnated on the rutile surface are also clearly seen. These three samples are of good cristallinity and particle size of at least 50 microns because of narrow peaks on corresponding XRD patterns.

The UV diffuse reflectance spectrum of TiO$_2$, expressed in Kubelka-Munk units are shown on Fig. 2. The intensitive absorption band in the UV region is ascribed to charge transfer from O$^{2-}$ to Ti$^{4+}$.The shoulder in the 500-800 nm area stands for the light admixtures of rare earth elements. The quantity of these elements is insignificant and they were not seen on the XRD pattern. The adding of Pt particles to the rutile surface results in shifting of adsorption band to the higher wavelength and subsequently in lowing of energy gap.

The TQ 150 Z2 lamp was used as a source of UV irradiation in the batch type reactor. The frequency content for it is shown on the Fig.3. The maximum radiant flux falls within UV-A (352 nm) and visible spectra (536 nm) content. As such the tested catalysts could be active both at UV and visible light.
Figure 1. XRD patterns of leucoxene sand, rutile and rutile modified with Pt (Q – quarts, R – Rutile, Pt – platinum).

Figure 2. UV-Vis spectra of leucoxene sand, rutile and rutile modified with Pt.
The curves for photocatalytic degradation of TCP in the presence of leucoxene concentrate, rutile and rutile modified with Pt particles (designated as Pt/rutile) are shown on Fig.4. The photolysis curve is also given as a reference.
It is clearly seen that all tested samples are not active in the photodegradation of TCP. It has been widely observed that the photocatalytic degradation of organic pollutants over TiO$_2$ only proceeds in the presence of oxygen. This is consistent with the recognized mechanism that $e^{-}$ and $h^{+}$ are formed in a pair, followed either by recombination to release heat, or migration into the surface to react with a suitable electron acceptor and donor [10]. Then, an increase in the surface concentration of the adsorbed O$_2$ (and organic substrate) on TiO$_2$ would result in enhancement in the rate of interfacial charge transfer and thus in the rate of organic degradation. However, a negative photocatalytic activity can be a result of a too small specific surface area. To check this assumption we have measured the BET area of leucoxene, rutile and Pt/rutile. For all three samples the obtained values were lower than
1 m$^2$/g. To increase the specific surface area rutile and Pt/rutile samples were crashed in ball mill; the XRD pattern for Pt modified rutile is shown on Fig.5. Only peaks which correspond to rutile could be seen, the average size of particles calculated from the broadening of the peaks using the Sherer equation is 13 nm. The second measurement of BET area gave 12 m$^2$/g. The obtained crashed samples of rutile and rutile modified with Pt were also tested in reaction of TCP photodegradation. The corresponding curves are given on Fig.6.

The crashed samples are more active in reaction. An improvement in specific surface area resulted in enhancement of charge carrier surface density and subsequently in the rate of TCP oxidation by h$^+$ or •OH.

The reaction rate constant has been calculated for as-prepared and crashed Pt modified rutile using Langmuir-Hishenwood model [11]. According to this model correlation between the reaction rate $k_{app}$ and concentration is given by the following equation:

\[
\ln \left( \frac{C_0}{C} \right) = k_{app}t 
\]

where $t$ stands for time (min), $C_0$ – the starting concentration of TCP and $C$ – concentration of TCP at the moment $t$. The calculated values of reaction rate are 0.004 min$^{-1}$ for Pt modified rutile and 0.01 min$^{-1}$ for crashed Pt modified rutile.

4. Conclusion

Three various samples were tested in the reaction of photodegradation of trichlorphenol. It was shown that rutile synthesized from leucoxene (Pizhemske deposit) could be used as photocatalyst in water treatment under the following conditions:

- the enhancement of specific surface area;
- using the particles of noble metals as dopants.

5. Acknowledgments

Agnes Szegedi and Jozsef Valyon are greatly acknowledged for help and useful discussions. The study was carried out with financial support of 12-T-5-1022 and N11-5-IP-249 programs of RAS.

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