Prospects of photocatalysis in diesel fraction purification

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Abstract. The photocatalysis process is widely used for removal of toxic chemical compounds from water and air. Oxides, sulfides of semiconductor materials are used as catalysts in photochemical processes, one of which is titanium dioxide. The manufacturing of an effective catalyst – nanotubes of titanium dioxide and the study of its physicochemical characteristics are considered in this paper. The behavior of titanium dioxide with various structures in the course of removing sulfur-containing organic compounds from diesel oil fractions is investigated. It is found out that titanium dioxide nanotubes (NT) are the most efficient catalysts for the photooxidation. Photocatalytic treatment of diesel fractions allows efficient and simple purification of oil products from unwanted components.

1. Introduction

Photocatalysis processes have been widely used to purify water and air from various toxic chemical compounds for a long time [1]. Oxides, sulfides of semiconductor materials (ZnO, SnO_2, Fe_2O_3, CdO, WO_3, In_2O_3, TiO_2, CdS, ZnS), oxides with deposited metals (Pt/TiO_2, $Rh/SrTiO_2$), dispersions with deposited oxides (RuO_2/TiO_2) and others are used as catalysts in photochemical processes [2, 3]. Titanium dioxide (TiO_2) is one of the widely used materials in photocatalysis processes due to its relative cheapness, non-toxicity, and efficiency. The photocatalytic activity of titanium dioxide is related to the relatively long lifetime of photogenerated charge carriers (about 250 ns) [4]. The main limitation of the titanium dioxide practical application in photochemical processes is the low quantum efficiency of the process due to the weak separation of photogenerated charge carriers and the need to use radiation only in the UV-range, because of the large band gap of TiO_2 (3.2 eV, 3.3 eV, 3, 0 eV) [5-8]. This property makes inefficient use of solar radiation, in whose spectrum the UV-part accounts for about 7%, while the visible range – 45% [9].

Titanium dioxide is a wide-gap semiconductor that exists in nature in the form of several crystalline modifications (anatase, rutile and brookite). Such crystalline forms as rutile and anatase are investigated in the most works on photocatalysis. With ultraviolet (UV) irradiation of titanium

dioxide, the absorption of a photon with an energy greater than the band gap (BG) results in the formation of an electron-hole pair. If the free charges do not recombine, they can migrate over the surface, where electrons are captured by titanium atoms, and holes – by surface OH-groups. Captured holes, interacting with surface OH-groups, give an OH• radical, and trapped electrons interact with O_2 and H_2O to form active radicals, such as O_2-, HOO • and HO •. Exactly these free radicals can oxidize the C-H bonds, what leads to the destruction of organic molecules.

Since the processes of photocatalytic oxidation proceed mainly on the surface of titanium dioxide, the use of TiO_2 nanoparticles, having a large specific surface area, seems to be the most logical approach for these purposes. The apparent advantage of nanoparticles in comparison with microparticles is the high probability of charge transfer to the catalyst surface. Due to the fact that the penetration depth of UV-light into TiO_2 particles is limited (~ 100 nm), only the outer surface is active one [10]. There are various morphologies of prepared TiO_2 nanoparticles: mostly nanotubes, nanowires, nanorods, and mesoporous structures [11]. To reduce losses and prevent possible recombination processes arising from the transition from one particle to another, it has been proposed to use nanostructures with 1D electron transport. These structures may include many modifications of titanium dioxide, such as nanotubes [12, 13], nanorods [14], and nanowires [15]. These 1D dimensional structures with direct electronic paths are expected to significantly increase the electron transport properties by eliminating grain boundaries arising from the use of nanoscale titanium dioxide particles. The use of structures with one-dimensional electron transport will facilitate a faster electron transfer process and a slower recombination process. In [16] is reported that the recombination processes occur 10 times slower in TiO_2 nanotubes (NT) than in nanoparticles.

In our opinion, the use of photocatalytic processes in the petrochemical industry for the oxidation of sulfur-containing compounds of petroleum and petroleum fractions is highly relevant, since the growth rates of production of high-sulfur oil increase every year.

Sulfur compounds in oils contribute to corrosion of equipment and poisoning of catalysts of the recycling process, cause corrosiveness in refined products, impair the quality and properties of the finished product and contribute to environmental pollution [17]. However, sulfur-containing organic oil compounds are used in petrochemical synthesis to obtain products of low-tonnage chemistry. They are used as extraction and flotation agents in hydro- and non-ferrous metallurgy and as plant growth phytoregulators in agriculture etc. Today there are many ways of extracting sulfur-containing compounds from oil and oil products: extraction, adsorption, oxidation, hydrotreatment, etc. However, each of these methods has many advantages but also disadvantages such as expensive reagents, large waste volumes and significant energy expenditures.

Photocatalytic methods of purification are devoid of these disadvantages and allow to achieve a relatively high level of removal of sulfur-containing compounds from oil fractions.

Hence, in [18] the process of diesel fuel desulphurisation using photooxidation over nanodispersed titanium dioxide is considered. It was found out that the degree of total sulfur removal is 61.9%. The use of a titanium dioxide (TiO2, Degussa P-25) catalyst [19] allows to remove 46.6 % of sulfur from waste tire pyrolysis oil.

It can be assumed that photocatalysis over titanium dioxide NT could increase the level of removal of sulfur compounds from oil fractions, since this inhibits various recombination processes during photo-oxidation and increases the lifetime of charge carriers.

The aim of this work is to obtain 1D dimensional particles of titanium dioxide (nanotubes) from industrially used titanium pigment (rutile pigment), to study the physicochemical properties of the obtained compounds, to consider the possibility of application of rutile pigments and TiO_2 nanotubes in photocatalysis processes in the purification of diesel fraction via removal of sulfur-containing compounds and assess the prospectivity of using this method for purification of heavy oil fractions.

2. Experimental part

We used titanium dioxide pigments from two different suppliers. Pigment No. 1 was titanium dioxide Chemours Ti-Pure R-706 (US) with the content of the rutile phase 98.5% (TiO_2-1). Pigment No. 2 was titanium dioxide Lomon R-996 (China) with the content of the rutile phase 95.0%, anatase 4.5%, and calcite 0.5% (TiO_2-2). We used also a 10W UV LED ultraviolet 385 nm high power led lamp light (Epistar, China). Physical properties of a diesel fuel used in the experiment are presented in table 1.

Table 1. Physical properties of a diesel fuel

Index	
Density, g/cm^3	0.83
Viscosity, mm^2/s at 20 ˚C	1.5
Boiling temperature, ˚C	180-360
Pour point, ˚C	-55 – -5
Flash point, ˚C	52
Sulfur content, %	0.22
Acid index	5
Iodine index	6
Coke value, %	0.1

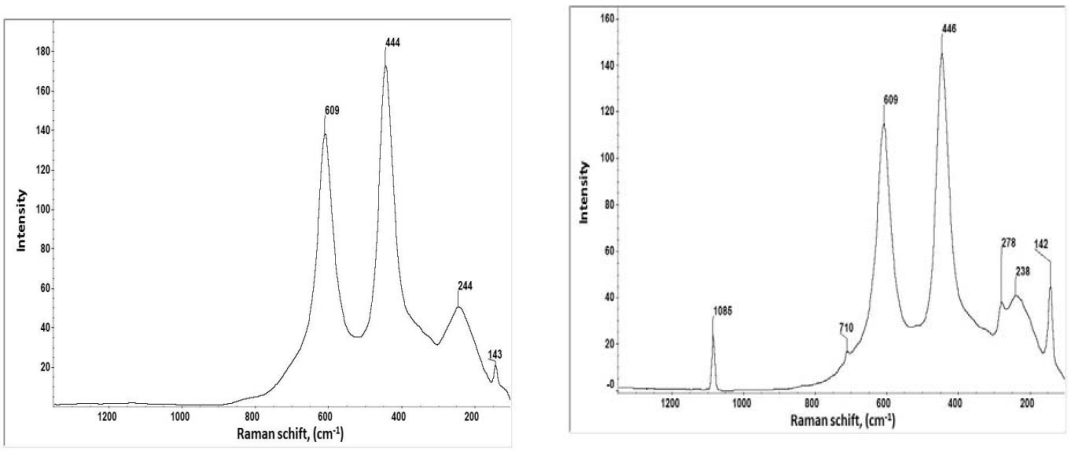
Physicochemical properties of rutile pigments and NT synthesized on their basis were investigated using the following methods:

- X-ray diffraction analysis using a Shimadzu XRD 7000 X-ray diffractometer. X-ray patterns were obtained with CuKα copper radiation by the Bragg-Bretagne scheme at 0.03 increments and exposure time 6 seconds – point, and angular range of 10°-80°. X-ray amorphous fraction was calculated using standard software supplied with the equipment.
- Infrared spectroscopy. IR-spectra were recorded using a Nicolet 5700 IR-Fourier spectrometer with FT-IR Raman module.
- High-resolution transmission electron microscopy. The size and shape of nanomaterial particles were measured using a JEM-100 CX II JEOL electron microscope.

The initial and resulted samples of titanium dioxide (NT) were analyzed by the methods of Raman spectroscopy, X-ray phase analysis, and high-resolution transmission electron microscopy (HR TEM). The catalytic photooxidation of sulfur-containing organic compounds (SCOC) of the diesel fraction was carried out in the presence of titanium dioxide. A diesel fraction with a sulfur content of 0.22 %wt. was used as a raw material, which was placed in a beaker in an amount of 100 ml, 1% (0.81 g) of the TiO_2 weight was added, all was thoroughly mixed on a magnetic stirrer, oxygen purge was turned on, and the mixture was irradiated by a light-emitting diode with a predetermined wavelength for 60 minutes. The irradiation wavelength was varied from 370 to 400 nm. Titanium dioxide was used in the form of pigments No.1, No. 2 and NT. At the end of the photooxidation process, the catalyst was removed from the diesel fraction by filtration or centrifugation. Oxidized sulfur-containing compounds from the diesel fraction were recovered by a single extraction by acetonitrile with water (5% vol.) at ‘the diesel fraction/acetonitrile-water’ volume ratio of 1/2. The sulfur content in the initial and refined diesel fractions was determined by method of burning in a lamp in accordance with the national standard GOST 19121-73.

3. Results and discussion

Figure 1 shows the Raman spectra of TiO_2 -1 and TiO_2-2 rutile pigment samples.



(a) (b)

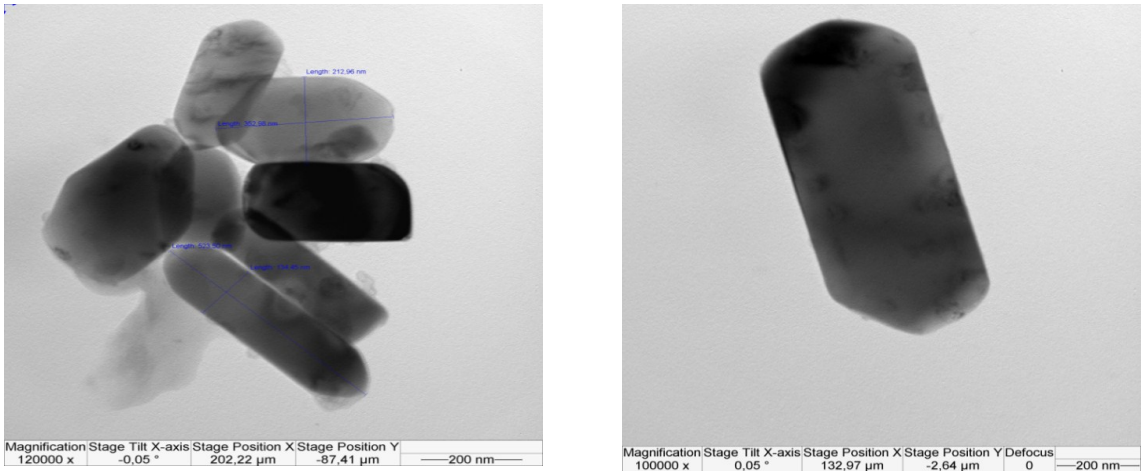
Figure 1. Raman spectra of TiO_2-1 (a) and TiO_2-2 (b) rutile pigments.

The obtained spectra are characterized by rutile structure. Rutile has four vibrational modes, characterized in work [20]. For the TiO_2-1 sample, the high-intensity bands were recorded at 227, 441, 609 cm^{-1}, and the low-intensity band – at 147 cm^{-1} (figure 1a).

The Raman spectrum of TiO_2-2 sample (figure 1b) is identical to the spectrum of TiO_2-1 sample (figure1a), except for the additional band in the frequency range of 1065 cm^{-1} attributed to the symmetric valent vibrations of O-C-O bond in calcium carbonate. Higher band intensity at a frequency of 145 cm^{-1} may indicate the presence of anatase phase in the TiO_2-2 sample.

X-ray patterns show that the TiO_2-1 sample contains only the rutile phase (crystallinity is 75.7%), and the sample TiO_2-2 (crystallinity 78.2%) contains three phases: rutile, anatase and calcite (in the ratio of 88:10:2 %, respectively).

The size and shape of the rutile pigments crystals are shown in the microphotographs of the samples (figure 2). According to microphotographs, the rutile pigments crystals have the form of a parallelepiped with dimensions in the range 250, 300 nm to 400, 500 nm.



(a) (b)

Figure 2. The TiO_2-1(a) and TiO_2-2(b) rutile pigments microphotographs.

To obtain the nanotubes, it was used the method proposed by Tomoko Kasuga with co-authors [21, 22]. According to this method, titanium dioxide is subjected to hydrothermal treatment in a

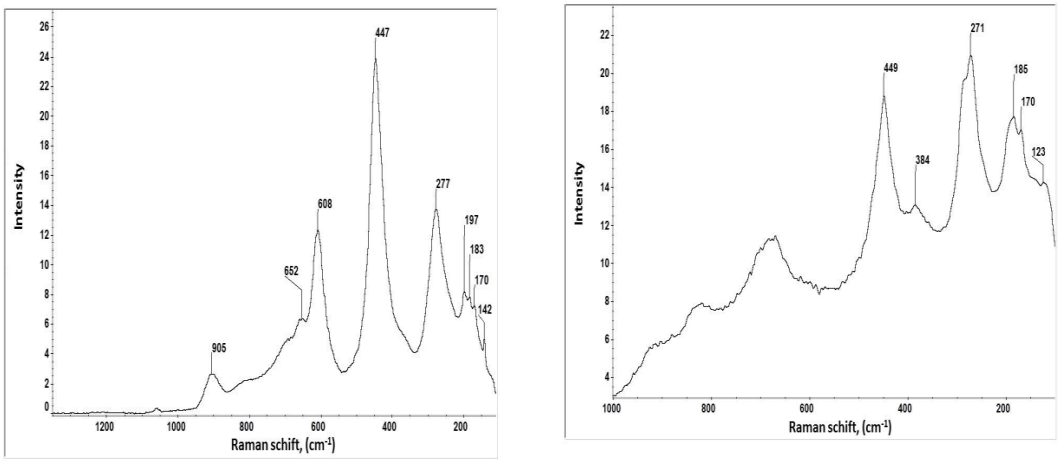
concentrated alkali solution (NaOH). Data on the effect of temperature, alkali concentration and reaction time on the process of nanotube formation are presented in table 2.

Table 2. Synthesis of Titanium Dioxide Nanotubes.

Synthesis	Initial material	Crystal modification	t, °C	T, hour	X-ray phase analysis	Raman-spectrum, cm^{-1}	HR TEM	C NaOH g/L
1	TiO_2-1	rutile	190	16	The crystalline phase is absent	607; 445; 249; 200	Very small particles, combined into round-shaped aggregates d=80-100 nm	12.5
2	TiO_2-1	rutile	190	6	The crystalline phase is absent. No peaks in small angles	607; 445; 249; 200	Very small particles, combined into round-shaped aggregates d=80-100 nm	12.5
3	TiO_2-1	rutile	160	16	No peaks in small angles	607; 445; 249; 200	A small amount of NT d = 8-12 nm, large aggregates of nanoparticles and very thin sheets	10
4	TiO_2-1	rutile	120 150	4 8	Blurred peaks in small angles 10.535; 24.608; 28.299	610; 447; 270; 193	NT d=10-16 nm	8
5	TiO_2-1	rutile	120 150	4 4	Blurred peaks in small angles 10.535; 24.608; 28.299	610; 447; 270; 193	NT d=10-16 nm	8
6	TiO_2-2	rutile, anatase, calcite	182	8	The crystalline phase is absent. No peaks in small angles	1085; 608; 445; 248; 200	Very small particles, combined into round-shaped aggregates d=80-100 nm	12.5
7	TiO_2-2	rutile, anatase, calcite	120 150	4 4	Blurred peaks in small angles 10.535; 24.608; 28.299	1085; 608; 445; 270; 200	NT d=10-16 nm	8

After the reaction's completion, the resulted product was washed with 0.1 M nitric acid (HNO_3) and distilled water until neutral reaction occurs.

According to the literature data [23], the formation of titanium dioxide nanotubes can be characterized using the methods of X-ray phase analysis, Raman spectroscopy and transmission electron microscopy. Hence, three blurred low intensity peaks should be presented on the X-ray patterns in the range of small angles 2θ (10.535, 24.608, 28.299), while according to the Raman spectroscopy data – a peak at the 270 cm^{-1}, what is confirmed by the results obtained. Figure 3 illustrates the Raman spectrum of the titanium dioxide NT sample obtained by the synthesis 7 and the synthesis 4.



(a) (b)

Figure 3. Raman spectrum of TiO_2-1 nanotubes (NT) sample, obtained by the synthesis 7 (a) and the synthesis 4 (b). The reaction temperature is 120-150°C, the reaction time is 8, 12 hours. The synthesis was carried out in an 8 M alkali solution.

A sufficiently intense peak at a frequency of 276 cm^{-1} characterizes the formation of titanium dioxide nanotubes. Low-intensity reflections with maximums in the range of angles 2θ 10.535; 24.608; 28.299, related to TiO_2 NT are present in the X-ray patterns of the samples obtained in syntheses 4, 5, 7, which is shown in figure 4 with the example of the sample obtained in the synthesis 7.

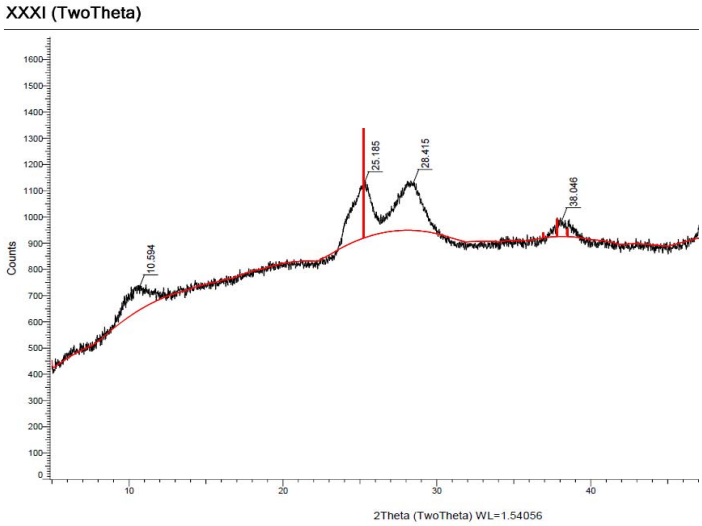
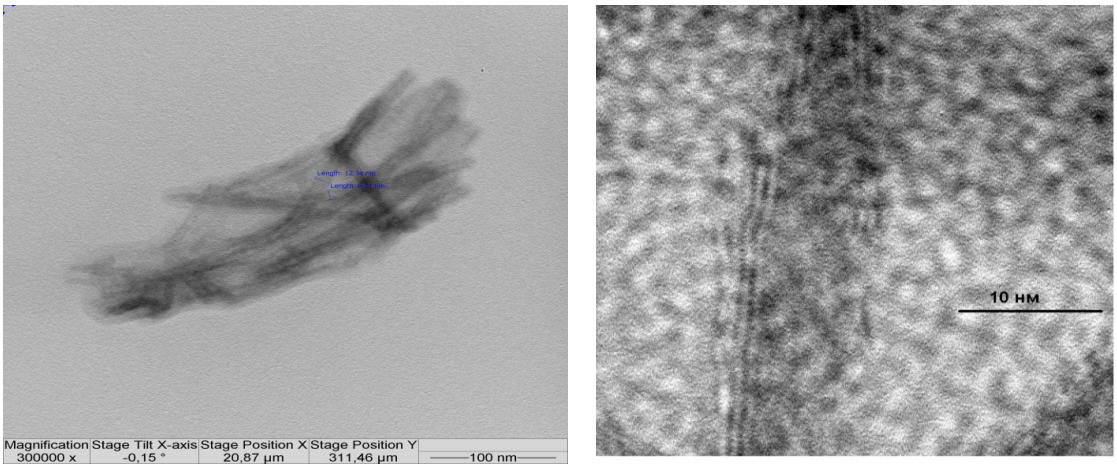


Figure 4. X-ray pattern of TiO_2 nanotubes (NT) sample.

Microphotographs of titanium dioxide nanotubes with the example of the sample obtained in synthesis 7 are shown on figure 5. Nanotubes have d=10-12 nm. Figure 5 b shows the laminated structure of obtained nanotubes.



(a) (b)

Figure 5. Microphotographs of TiO_2 NT.

A mechanism explaining the formation of titanium dioxide particles with the morphology of nanotubes was first proposed in [24, 25]. It is assumed that large crystalline particles of titanium dioxide in the presence of alkali (sodium hydroxide) at the temperature less than 120 °C are converted into sodium titanate having a laminated structure, which subsequently is stratified into individual crystalline layers loosing stability with temperature increasing and rolling up into rolls (tubes). After

product's treatment with solutions of mineral acids, sodium cation is removed from their structure and individual crystal nanotubes are formed.

According to the obtained results, the conditions for the TiO_2 nanotubes (NT) formation are following: the alkali concentration is less than 8 mol/L (8M); the reaction temperature is not higher than 120-150 °C; the reaction time is not less than 4 hours.

Based on analysis of the physicochemical characteristics of the rutile pigments TiO_2-1 and TiO_2-2 and the obtained TiO_2 nanotubes, there was a catalytic photooxidation of the diesel petroleum fraction in their presence. The results of catalytic photooxidation of the diesel fraction are given in table 3.

Table 3. Results of the diesel fraction purification via catalytic photooxidation

Wavelength of UV-light, nm	Sulfur content, %wt.			
	in raw material	in purified, Kt: TiO_2 -1	in purified, Kt: TiO_2 -2	in purified, Kt: HT TiO_2
370-375	0.22	0.17	0.19	0.12
380-385	0.22	0.09	0.12	0.03

The process temperature 20 ±2 °C; volume of raw material 100 mL, catalyst content 1 wt %.

It follows from the analysis data presented in table 3 that the sulfur content in the oil product decreases when treating of the diesel fraction by UV-light in the presence of titanium dioxide. The sulfur content in the diesel fraction decreased from 0.22 to 0.09 wt% during UV-light treatment at a wavelength of 380-385 nm in the presence of a TiO_2-1 catalyst and from 0.22 to 0.12 wt% in the case of use of TiO_2-2. The maximum decrease in sulfur content in the diesel fraction is observed in the case of titanium dioxide nanotubes used as a catalyst under UV-light irradiation.

Hence, the sulfur content of the refined diesel fraction was 0.03 wt% under UV-light irradiation at a wavelength of 380-385 nm. Thus, titanium dioxide nanotubes exhibit a higher activity during the photocatalytic treatment of the diesel fraction with the purpose of sulfur-containing compounds removal due to their ability to transfer electrons more rapidly and to slow down the recombination processes.

4. Conclusion

The conditions of formation of TiO_2 nanotubes (NT) have been determined: the alkali concentration is lower than 8 mol/L (8M); the reaction temperature is not higher than 120-150 °C; the reaction time is no less than 4 hours. The processes of catalytic photooxidation of a diesel oil fraction, using titanium dioxide in the form of rutile pigments and nanotubes have been investigated. It has been found out that titanium dioxide in the form of nanotubes is the most effective catalyst. Thus, it has been established that the photocatalytic treatment of diesel fractions makes possible an efficient and simple removal of unwanted components such as sulfur-containing organic compounds from oil products.

Acknowledgments

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