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Influence of TiO₂ State on Oxidative Delignification of Aspen Wood and Wheat Straw

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The influence of preparation methods on structural characteristics of TiO₂ catalysts was studied by the XRD, SEM, BET, DTA-DSC, FTIR techniques.

Catalytic activity of obtained titanium dioxide samples was compared in reaction of oxidative delignification of aspen wood and wheat straw by hydrogen peroxide in acetic acid- water medium. The use of titanium dioxide in rutile modification allows to produce a cellulose product with lower content of a residual lignin, as compared to TiO₂ in anatase modification. The increase of surface area of the TiO₂ catalyst reduces its activity in wood and wheat straw delignification.

Keywords: TiO₂ catalyst, oxidative delignification, aspen wood, straw wheat, hydrogen peroxide, cellulose.

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Влияние состояния TiO₂ на окислительную делигнификацию древесины осины и соломы пшеницы

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Методами РФА, СЭМ, БЭТ, ДТА-ДСК, ИКС изучено влияние способов получения катализаторов TiO₂ на их структурные характеристики. Сопоставлена каталитическая активность полученных образцов диоксида титана в реакции окислительной делигнификации древесины осины и соломы пшеницы пероксидом водорода в среде «уксусная кислота–вода». Использование диоксида титана в модификации рутил позволяет получить целлюлозный продукт с более низким содержанием остаточного лигнина, чем при использовании TiO₂ в модификации анатаз. Увеличение удельной поверхности катализатора приводит к уменьшению степени делигнификации древесины осины и соломы пшеницы.

Ключевые слова: катализатор TiO₂, окислительная делигнификация, древесина осины, солома пшеницы, пероксид водорода, целлюлоза.

Introduction

The process of lignocellulose biomass delignification in the “hydrogen peroxide-acetic acid-water” mixture is considerably accelerated in the presence of different catalysts [1, 2]. Sulfuric acid can act as a catalyst of wood [3] and wheat straw [4] oxidative delignification processes. But, at the same time, H₂SO₄ promotes the hydrolysis of polysaccharides decreasing of the yield of cellulose product. Besides, H₂SO₄ catalyst has such technological disadvantages as toxicity and corrosion activity.

Some complexes on the basis of metals of variable valency, for example so-called polyoxometalates, can promote the process of wood delignification by oxygen [5, 6].

Catalytic properties of a number of tungsten and molybdenum compounds (Na₂WO₄, Na₂MoO₄, H₃PW₁₂O₄₀, CuSO₄, H₂SO₄, Na₂WO₄-CuSO₄, Na₂MoO₄-CuSO₄, H₃PW₁₂O₄₀-CuSO₄, H₃PW₁₂O₄₀-H₂SO₄, Na₂WO₄-H₃PW₁₂O₄₀-H₂SO₄) were studied in the processes of wood acetic acid delignification [7]. However the practical use of these catalysts is complicated by their high cost and complexity of regeneration for a reuse.

The more technologically convenient solid TiO₂ catalyst promotes effective removal of a residual lignin from technical cellulose in the presence of such oxidants as hydrogen peroxide and oxygen

[8–9]. Also TiO₂ can catalyze an oxidative delignification of wood by H₂O₂ [10]. Advantages of TiO₂ application as delignification catalyst are stipulated by the absence of corrosion activity and toxicity, by its availability, low cost and lack of need for its regeneration. It worth to note, that catalytic properties of TiO₂-based materials are sensitive to the method of their producing [11].

The present paper describes the influence of preparation methods on structural characteristics of TiO₂ and on its catalytic properties in the delignification of aspen wood and wheat straw with the acetic acid – hydrogen peroxide – water mixture.

Experimental

TiO₂ preparation

Two methods are usually used for TiO₂ obtaining: hydrolysis or sedimentation by alkalis from solutions of chloride or sulfate titanium (IV), with the subsequent washing, drying and heat treatment at a temperature not below 400–500 °C or by thermal hydrolysis of titanium salts solutions [12].

In the present study the synthesis of titanium dioxide was carried out by hydrolysis of ammonia solution of titanium tetrachloride with the subsequent calcination of a titanium (IV) hydroxide according to [13].

The necessary amount of TiCl₄ was slowly added to a chemical glass with distilled water and the mixture was boiled within 10 minutes. Then a solution was cooled up to the temperature of 70–80 °C and NH₄OH was added up to full sedimentation of Ti(OH)₄. Precipitate was filtered on Byukhner's funnel and washed out by hot water, up to disappearance of reaction on chlorine ions. Obtained paste of titanium hydroxide (IV) was then transferred to Petri's dish and dried up in muffle at 110 °C up to the constant weight. The dried-up precipitate was placed to the porcelain boat and calcinated in the muffle furnace at various temperatures within one hour.

For obtaining TiO₂ samples in the rutile modifications, the dried-up precipitate was calcinated at 800 °C within one hour, then crushed in an agate mortar, washed out by water up to disappearance of reaction on chlorine ions and calcinated at 1000 °C within 1,5 hours. The yield of titanium dioxide in rutile modification was 98.5-99.5 % weight.

In some cases the additional mechanical activation of titanium dioxide was carried out in AGO-2 planetary mill. The time of activation was varied from 10 to 30 min.

Catalytic delignification of wood and wheat straw

Air dry sawdust (fraction 2-5 mm) of aspen wood (*Populus tremula*) and wheat straw were used as the initial raw materials. The chemical composition (% wt. on abs. dry raw material) of aspen wood was: 47.3 cellulose, 22.9 lignin, 23.7 hemicelluloses, 3.7 extractive substances; of wheat straw: 39.2 cellulose, 20.6 lignin, 30.7 hemicelluloses, 5.5 extractive substances.

Delignification of wood sawdust and wheat straw was carried out in a glass reactor of 250 cm³ volume supplied by mechanical stirrer, condenser and thermometer. The following reaction conditions were used: temperature 100 °C, CH₃COOH concentration – 25 % wt., H₂O₂ – 4 % wt., TiO₂ catalyst – 1 % wt., time – 4 h. In order to reduce the diffusion limitation, the high liquid to solid ratio (15) and intensive agitation (700 rpm) were used.

Such parameter, as the residual lignin content in cellulose product was used to evaluate the delignification activity of TiO₂ catalysts. Cellulose product yield was estimated by the weight method

and calculated as follows: $\text{yield} = (m/m_0) \times 100 \%$, where m is the mass of abs. dry cellulose product (g), m_0 – the mass of abs. dry wood or straw.

Analysis of catalysts and products

X-ray diffraction analysis of TiO₂ catalysts was carried out with Dron-4 diffractometer using a Cu-K_α source. The mass of samples was 1,0–1,5 mg.

The electron microphotographs were obtained by a SEM TM-1000 HITACHI (Japan).

Specific surface area of the TiO₂ catalysts was determined by the BET single-point method using nitrogen adsorption at 77 K at a relative pressure $P/P_0 = 0.2$ with the analyzer “Sorbometr – M”. The mass of analyzed samples was 50–60 mg.

The thermal analysis was carried out with thermal analyzer STA 449 F1 *Jupiter* (NETZSCH firm) in the range of temperatures 20-1000 °C. The speed of temperature rise was 10 degrees/min. The mass of samples was 2.6 mg.

Infrared spectroscopy analysis (FTIR) of TiO₂ catalysts was carried out in transmission mode. The spectra were recorded with Vector-22 spectrometer in the 400-4000 cm⁻¹ wavelength range, using 3 mg sample in KBr matrix. Spectral data were processed by program OPUS/YR (version 2.2).

Standard chemical methods were used for analysis of cellulose products composition [14]. The cellulose content in solid products was defined by Kurschner method, the lignin content – by hydrolysis of the sample with 72 % mas. of sulfuric acid at 20 °C for 2.5 h (Komarov’s modification), hemicelluloses content – by McKein and Shoorly method using the hydrolysis by 2 % HCl at 100 °C during 3 h.

Results and discussion

Influence of calcination temperature and of mechanical treatment in AGO-2 planetary mill on a phase composition and specific surface area of obtained TiO₂ samples was studied (Table 1).

The titanium hydroxide sample, which has been dried at 110 °C represents mix of amorphous and crystal modification of anatase. This conclusion is confirmed by data of X-ray diffraction analysis (Fig. 1) [15]. This sample has a maximum value of specific surface area – 260 m²/g (Table 1).

Table 1. Phase composition and specific surface area of obtained TiO₂ samples

№	Temperature of calcinating, °C	Phase composition	Time of treatment in AGO-2, min	Surface area, m ² /g
1	110	TiO ₂ (anatase)	–	260
2	300	TiO ₂ (anatase)	–	111
3	500	TiO ₂ (anatase)	–	89
4	1000	TiO ₂ (rutile)	–	less 1
5	1000	TiO ₂ (rutile)	10	2
6	1000	TiO ₂ (rutile)	15	7
7	1000	TiO ₂ (rutile)	20	6
8	1000	TiO ₂ (rutile)	30	11

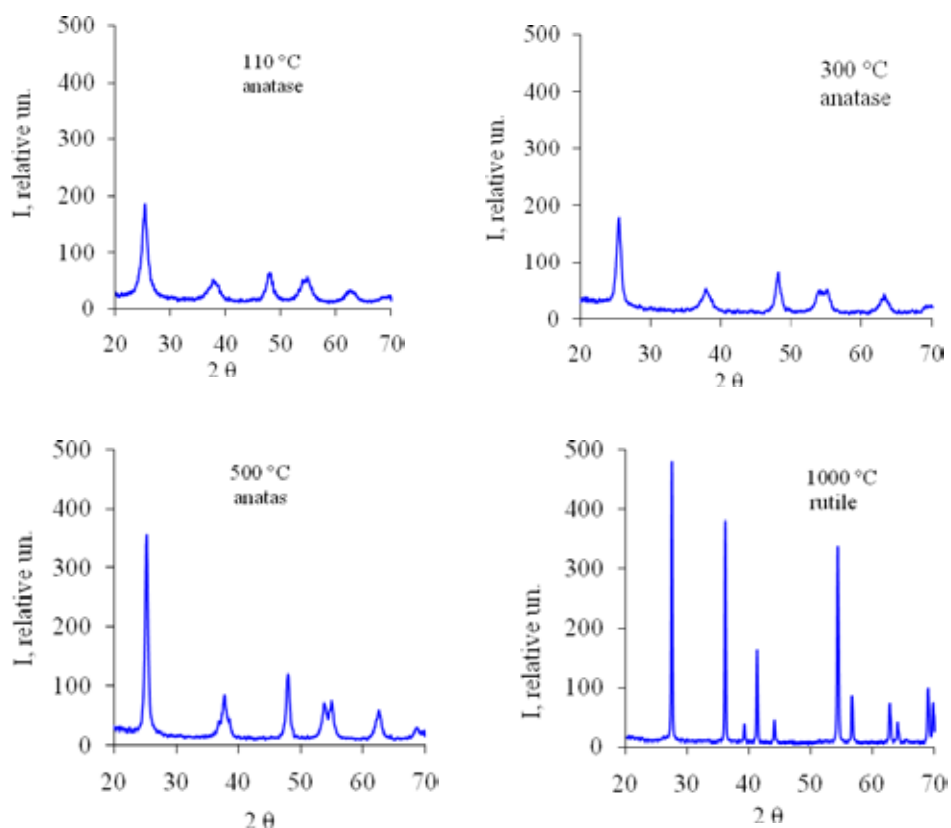


Fig. 1. X-ray diffraction pattern of TiO₂ samples, obtained at different temperatures

The increase of treatment temperature from 100 to 1000 °C intensifies the dehydration processes with transformation of amorphous hydrated titanium dioxide into crystalline anatase with following transformation of anatase into rutile form of TiO₂ and recrystallization of the rutile. The increase of calcination temperature reduces the specific surface area of titanium dioxide.

According to SEM data the crystals of TiO₂ in a rutile modification have a spherical form (Fig. 2). Treatment of titanium dioxide sample in rutile modification in a planetary mill increases the surface area of samples from 4 to 27 times, depending on the duration of treatment (Table 1). The destruction of spherical particles of TiO₂ was observed after mechanical treatment (Fig. 2).

The degree of particles grinding is increasing with a time of treatment.

X-ray diffraction pattern of all TiO₂ samples, treated in a planetary mill, have a similar form typical to rutile modification of titanium dioxide.

According to thermal analysis data, the most high loss of weight (20,64 %) was observed in the case of TiO₂ sample, obtained by thermal treatment at 110 °C (Fig. 3).

TiO₂ samples calcinated at 300 and 500 °C lose only 8.86 and 8.75 % of weight respectively. Exothermic effect at temperature about 800 °C may be connected with the structural transformation of anatase to rutile.

IR-spectra of TiO₂ samples of anatase and rutile modifications were compared (Fig. 4 and 5). The absorption bands corresponding to deformation (1040-1140 cm⁻¹) and stretching (3200-3400 cm⁻¹)

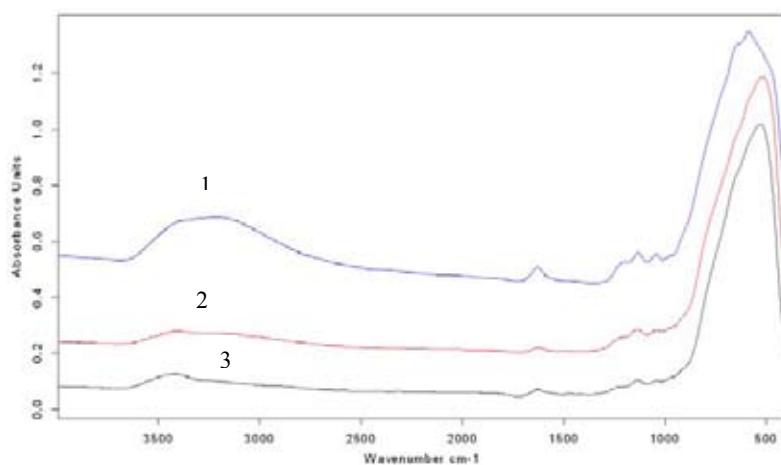


Fig. 4. IR – spectra of samples of titanium dioxide in anatase modification, obtained at 110 (1), 300 (2) and 500 °C (3)

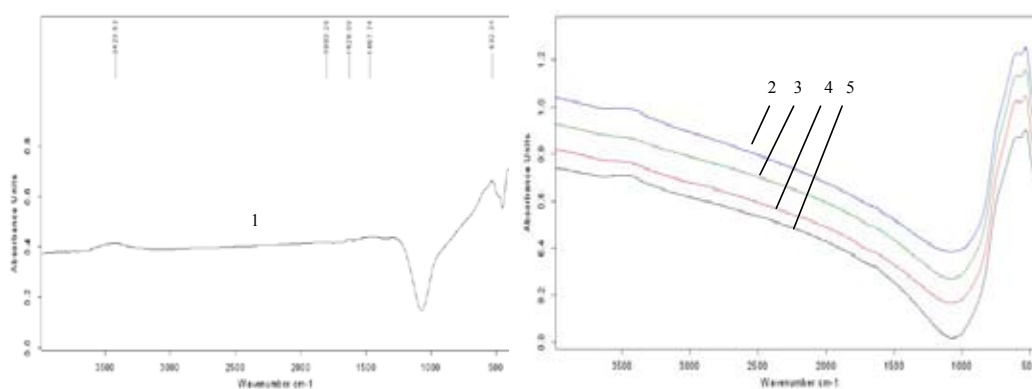


Fig. 5. IR – spectra of samples of initial titanium dioxide in rutile modification (1) and after mechanical treatments during 10 min. (2), 15 min. (3), 20 min. (4) and 30 min. (5)

Catalytic properties of TiO₂ samples in anatase and rutile modifications were compared in the process of aspen wood and wheat straw oxidative delignification by H₂O₂.

High catalytic activity of titanium dioxide in the oxidation processes with hydrogen peroxide is explained by its ability to initiate the formation of radicals •OH and •OOH from H₂O₂ [16]. Being formed radicals participate in reactions of oxidative destruction of lignin [17].

Catalytic experiments were made at earlier established optimum delignification parameters [18]: temperature 100 °C, H₂O₂ – 4 % wt., CH₃COOH – 25 % wt., TiO₂ – 1 % wt., liquid/solid ratio – 4, time – 4 h. Results of the accomplished studies are presented in Tables 2 and 3.

The obtained data show that the use of titanium dioxide catalyst in rutile modification gives cellulose product with lower content of residual lignin, as compared to TiO₂ in anatase modification.

Samples of titanium dioxide in anatase modification which were obtain at temperatures 110 °C, 300 °C and 500 °C have a rather high surface area (260, 111 and 89 m²/g). The reduced catalytic

Table 2. Influence of TiO₂ catalysts and conditions of aspen wood delignification on the yield and composition of cellulose products

Sample number	TiO ₂ modification	TiO ₂ treatments	Yield of cellulose product, % wt.*	Composition of cellulose product, % wt.**		
				Cellulose	Lignin	Hemicelluloses
1	Anatase	110 °C	74.5	79.4	12.2	8.1
2	Anatase	300 °C	68.6	77.6	9.8	12.3
3	Anatase	500 °C	66.3	86.3	7.8	5.6
4	Rutile	1000 °C	50.8	91.8	1.6	6.3
5	Sample 4	AFO-2, 10 min.	53.2	89.4	3.8	6.5
6	Sample 4	AFO-2, 15 min.	58.4	87.7	4.2	7.8
7	Sample 4	AFO-2, 20 min.	56.7	88.0	3.9	7.8
8	Sample 4	AFO-2, 30 min.	65.8	85.9	5.6	8.2

* on abs.dry wood

** on abs.dry cellulose product

Table 3. Influence of TiO₂ catalysts and conditions of wheat straw delignification on the yield and composition of cellulose products

Sample number	TiO ₂ modification	TiO ₂ treatments	Yield of cellulose product, % wt.*	Composition of cellulose product, % wt.**		
				Cellulose	Lignin	Hemicelluloses
1	Anatase	110 °C	72.2	71.4	14.8	9.8
2	Anatase	300 °C	68.4	75.5	10.2	10.3
3	Anatase	500 °C	66.3	76.8	8.4	10.8
4	Rutile	1000 °C	54.0	81.0	4.2	10.8
5	Sample 4	AFO-2, 10 min.	54.8	80.5	5.2	10.3
6	Sample 4	AFO-2, 15 min.	62.9	78.2	6.4	11.4
7	Sample 4	AFO-2, 20 min.	64.6	77.4	6.8	11.8
8	Sample 4	AFO-2, 30 min.	65.7	78.1	7.1	10.8

* on abs.dry straw

** on abs.dry cellulose product

activity of these samples in oxidative delignification of aspen wood and wheat straw may be explained by two reasons.

Probably, the developed porosity of anatase samples reduces their catalytic activity in delignification processes owing to strengthening of diffusion limitations inside pores. The heat treatment of titanium dioxide at 1000 °C promotes its transformation to rutile modification, reduces its surface area and increases the size of pores. The latter results in the reduction of diffusion limitation inside pores and increases a catalytic activity of TiO₂ in delignification processes.

Besides that, a higher concentration of hydrogen groups on the surface of anatase modification of TiO₂ as compared to its rutile modification can prevent the formation from H₂O₂ the radical species (•OH and •OOH) active in destruction of lignin.

Conclusion

The influence of thermal and mechanical treatments of titanium dioxide on its structural characteristics and catalytic properties in oxidative delignification of aspen wood and wheat straw was studied.

It was determined that the increase of temperature treatment from 110 to 1000 °C results in the reduction a specific surface area of TiO₂ from 260 m² /g to less 1 m² /g and promotes the transition of anatase modification to rutile modification.

Mechanical treatment of titanium dioxide in the form of rutile using planetary mill AGO-2 increases its specific surface area from 4 to 27 times, depending on the duration of treatment.

It was found, that the best catalytic activity in aspen wood and wheat straw delignification possesses has a titanium dioxide in rutile modification with a low surface area, obtained at 1000 °C.

The use of this catalyst made it possible to obtain from aspen wood and wheat straw the cellulose products with a high yield and with the low content of a residual lignin (1.6 and 4.2 % wt. respectively).

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