Rutile-anatase Composite Catalyst Formed by Coupling Anatase and Rutile Particles

A. Kalashnikova, N. Nikolenko*, J. Kalashnikov, A. Kostynyuk

Faculty of Silicate Technology, Ukrainian State University of the Chemical Engineering, Dniepropetrovsk, 49005, Ukraine
*Corresponding Author: n_nikolenko@ukr.net

Abstract Anatase-type TiO₂ particles were formed on a surface of rutile particles by thermal crystallization from amorphous titan oxyhydroxide that was obtained from the aqueous solution of TiOCl₂ using urea hydrolysis. Special attention was paid to obtain rutile-anatase composite with reproducible physico-chemical properties by control of synthesis parameters. Catalytic activity of the synthesized composite was studied on photoinduced oxidation of formaldehyde vapours in a flow reactor.

Keywords Titanium Dioxide, Rutile-anatase Composite, Formaldehyde, Photocatalytic Oxidation Process

1. Introduction

The investigations of catalytic processes induced by light on semiconductors’ surface have drawn attention of many researchers because of promising perspectives of catalytic technology [1]. Both fundamental and applied researches have the common problem of choosing optimum semiconducting material. The main task is to find the material which is the most active and has the highest degree of light energy use [2].

At present, titanium dioxide is considered to be one of the best photocatalysts which is industrial product as well as product of synthesis in many research laboratories. It is also well known, that anatase form of titanium dioxide demonstrates the highest photocatalytic activity. The cause of this phenomenon remains unclear because of a number of exceptions. For example, one of the best industrial photocatalysts – titanium dioxide Degussa P-25 – includes 20% of rutile and 80% of anatase modifications. A number of authors explain high photocatalytic activity of rutile-anatase structure by phase boundary, which favors to increase concentration of electron-hole charge carrier by inhibition of the process of their recombination [3].

In our opinion, studies on influence of phase boundary in titanium dioxide on its photocatalytic properties can be carried out by means of rutile-anatase composites. The question is not mechanical mixture of anatase and rutile particles, but such a structure when on the surface of relatively large particles of rutile (or anatase) microparticles of titanium dioxide with rutile (or anatase) crystal structure are formed. During synthesis of this composite it is possible to control effectively relation of two crystalline phases just on particle surface, i.e. where photocatalytic redox process of destruction and oxidation of organic compounds take place.

The present work is aimed at developing rutile-anatase composite process by titanium(IV) oxyhydroxide precipitation on the surface of rutile particles at controlled degree of mother liquor supersaturation with its subsequent dehydration and calcination to form crystalline phase of anatase. To obtain composites with reproducible physico-chemical properties during synthesizing special attention was paid to control of its basic parameters. Concentrations of metal ions, hydrogen and rutile particles, the degree of mother liquor supersaturation, the time of hydroxide ageing, temperature and time of composite drying and calcination were considered as above mentioned parameters.

By way of working hypothesis for producing highly active photocatalyst we consider the task of obtaining the composite in which some part of rutile particles surface would remain free of anatase microparticles. The point is that light extinction coefficient of rutile in the near-ultra-violet region is higher than that of anatase. This is explained by the fact that the width of rutile forbidden band is smaller than anatase. Therefore, light absorption band by rutile surface is partially shifted from UV-region into visible spectrum. It was assumed that absorption of light quantum by rutile would favour increasing concentration of free charge carrier not only in rutile structure, but in anatase “superstructure” of composite particle. A similar hypothesis about the possibility of enhancing visible-light-induced photocatalytic activity by means of the composites of different catalysts based on the coupling suitable wide and narrow band-gap semiconductors also have been expressed authors [4].

In this paper the synthesis of rutile-anatase composite catalyst with 10% content of anatase is described. Catalytic properties of the substance are investigated by an example
of photoinduced oxidation of formaldehyde vapours in model flow reactor.

2. Materials and Methods

Modification of rutile surface by anatase particles was carried out by precipitation of titanium(IV) oxyhydroxide in presence of rutile suspension. To 5.00 g of rutile sample were added 100 ml 1 M solution of acid (HCl or H2SO4) and 5.50 ml 1.140 M solution of TiOCl2. Precipitation by aqueous ammonia was conducted at room temperature, precipitation by urea was carried out by heating up to 70°C. Conditions of synthesis, washing, drying and calcination of the precipitate are described in the article.

Synthesis of rutile as a composite substrate was carried out by calcination of titanium(IV) oxyhydroxide at 900°C for 10 hours. Titanium(IV) oxyhydroxide have been prepared by mixing TiOCl2 and NH4OH solutions at 298 K and pH=1.1,0 in a reactor with stirrer. Before calcination precipitate of TiO(OH)2 was filtered and extensive washed with deionized water, isopropyl and amyl alcohols. The particle size distributions were determined by sedimentation analysis. A single-mode distribution centered at 13 µm was found which leads to an average equivalent radius of rutile particles of 21±2 µm.

Methodology of experiments on photocatalytic oxidation of formaldehyde has been described in [5]. The study was performed in a model flow photoreactor. Schematic representation of used reactor is shown in fig. 1.

Figure 1. Scheme of facility for study of photocatalytic oxidation of formaldehyde. 1-flasks with sulfuric acid; 2-containers with granulated activated carbon and CaCl2; 3-control vessel; 4,5,7-flow meters; 6-gas mixing flask; 8-evaporator; 9-flow photoreactor.

The morphologies and microstructures characterizations were performed on a Selmi scanning electron microscope (SEM). The crystalline phase composition was analysed by X-ray diffraction (XRD) using a X'Pert Powder instrument fitted with a hemispherical analyzer with CuKα radiation. Thermal studies (DTA-DSC, TGA) were performed on SDT Q600 thermal analyzer.

3. Results and Discussion

A special attention in modification of rutile surface by anatase particles and obtaining of the rutile-anatase composite with reproducible properties was paid to control of key-parameters of all stages of synthesis process. This process was regarded as sequence of the following stages: a) preparation of rutile suspension in titanium(IV) salts solutions; b) precipitation of titanium oxyhydroxide at controlled changes of mother liquor supersaturation; c) ageing of titanium oxyhydroxide in mother liquor; d) washing, drying and calcination of obtained composite.

3.1. Standardization of Initial Parameters of Synthesis Process

It is known for certain that ions of titanium(IV) in aqueous solutions are subjected to hydrolysis and polymerization. In diluted chloride solutions at C(H+) > 0.1 M titanium ions are mainly in the form of TiO2+ [6]. With the increase of concentration poly nuclear cationic complexes are formed. According to the authors [7] in 0.02 M titanium(IV) solutions complexes with the composition [(TiO)x(OH)12]4+ become predominant form. On account of Coulomb repulsion the union of TiO2+ or TiO(OH)2+ cations into poly nuclear complex appears to be unlikely. Therefore, hydroxo-complex polymerization is usually regarded as successive attachment of uncharged (neutral) particles to charged complex particles, for example: [TiO(OH)2]0 or [(TiO)x(OH)2x]0, where x is polymerization degree. Apparently, due to low concentration of neutral complexes in strong acidic solutions the rate of establishing equilibrium for the process involved is rather low. In chemistry of complex compounds low rate of ligand-exchange reactions for ions of titanium(IV) is explained by their low lability. Large positive charge of cation and its relatively small radius are considered to increase activation energy of replacement reaction which results in decreasing rate of intraspheric ligand exchange into hydroxide ions or water molecules from solution environment.

Thus, for standardization of initial composition of titanium(IV) hydroxo-complexes after dilution or change of solution acidity it is necessary to wait for hydrolytic equilibrium to be completed. Otherwise, hydroxide deposition will proceed at uncontrolled composition of titanium complexes; this can influence the parameters of solid phase nucleus formation.

Another no less important parameters of composite synthesis, to our opinion, appears to be adsorption of titanium hydroxo-complexes on rutile surface. It is known, that multicharged ions are able to be specifically absorbed on oxide surfaces. Such adsorption can be regarded as the process of surface hydrolysis when a part of coordination sphere ligands are replaced by OH-groups on oxide surface.
According to that there must not be any principal differences for auto adsorption \([\text{TiO}_x\text{(OH)}_{2x}]^z\) on rutile surface. Surface
of formed hydroxo-complexes can be considered as crystallization centre of titanium hydroxide phase.
Apparently, at various content of such crystallization centre
on the surface of rutile particles composites with different
distribution of hydroxide particles both according to their
number and size can be formed. That is why for
standardization of initial conditions for composite synthesis
in the solution of rutile powder suspension and titanium salt,
adsoption equilibrium should be complete.

Invariability of solution acidity may serve as common sign
of attaining hydrolytic and adsorption equilibrium. To
confirm this conclusion experimentally we carried out
studies on dynamics of acidity change in 1 M solution of
hydrochloric acid in quantity of 100 ml when 5 g of rutile
powder and 5.5 ml of 1.14 M TiOCl₂ solution with initial
pH=0 was added. It was found that after quick increase of pH
(by 0.4 unit) caused by hydrolytic processes proceeding on
titanium oxide surface, during the following 5 hours pH of
the solution increases by 0.28 unit more. This can be
explained by slow rate of hydrolysis process and adsorption
of titanium(IV) cation complexes.

Therefore, to standardize initial parameters of synthesis
solution of titanium(IV) salt after dilution, change of acidity
and sample addition TiO₂ should be preliminary kept for no
less than 5 hours for completing hydrolytic and adsorption
equilibrium.

### 3.2. Standardization of Titanium Oxyhydroxide
Precipitation and Ageing Parameters

It is well known that appearance of a new phase is possible
in metastable system which is disturbed from the equilibrium
as a result of changes in chemical composition (oversaturation method) or physical action (e.g., temperature
and/or pressure in hydrothermal method of precipitation).
The formation of a new phase begins with the appearance of
so-called critical nuclei. It is known that if there is seeding
agents the probability of heterogenous nucleation as
contrasted to by homogeneous nucleation is considerably
increased. In such cases the crystallization goes on a surface
of seeding agents.

On regularities of heterogenous nucleation we have
developed method for obtaining rutile-anatase composite by
titanium(IV) oxyhydroxide precipitation in presence of rutile
suspension under conditions of controlled change of mother
liquor acidity [8]. In result of preliminary test it was found
that TiO(OH)₂ precipitation by ammonia hidroxide from
titanium(IV) hydrochloride solutions at pH~2 lead to
formation of a sol of titanium(IV) oxyhydroxide. made that
The reason of sol formation in this process is homogenous
precipitation when nuclei of oxyhydroxide particles are
formed not on the rutile particles surface in solution volume.
During nuclei growth because of high charge and small mass
they remain in the solution forming stable sol.

According to classical theory of precipitation formation,
in order to retard nucleation in solution volume it is
necessary to decrease rate of precipitant agent addition and
thus to lower degree of mother liquor supersaturation. As
stated above, heterogenous nucleation is in fact of process of
polymolecular adsorption of uncharged hydroxo-complexes
since only these particles don’t suffer considerable
electrostatic repulsion when approaching charged surface of
oxide. Taking into account relatively low rate of titanium
ions hydrolysis we conclude that the lower the rate of
precipitator addition, the higher the degree of fit ions
transformation into neutral form \([\text{TiO}_x\text{(OH)}_{2x}]^0\) and the
more likely their adsorption on rutile surface.

Decrease of hydroxide precipitation rate was realized by 2
methods: by gradual (stepping) addition of precipitator and
by method of arising reagents. In the first case ammonia
solution was added in suspension solution by small portions
in such a way that the value of solution pH changed by no
more than 0.1 unit during 5 hours (the time for the
equilibrium of titanium ions hydrolysis to be completed).
The change in acidity was done within the interval from 0.6
(begining of hydroxide precipitate formation) to 2.0 units.

Urea was added in the titanium(IV) solution for realization
of arising reactants way. As it’s known, during urea
hydrolysis concentration of hydrogen ions in a solution
gradually decreases:

\[
(\text{NH}_2\text{CO})_2\text{O} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{HCO}_3^- + 2\text{NH}_4^+.
\]

It slowly displaces equilibrium of hydrolysis of metals
cations, owing to particles of a hydroxide solid phase are
formed at low supersaturation degrees. In both cases
precipitation carried out from sulfate solutions that allowed
to prevent probable precipitation of titanium hydroxide in the
rutile form. As is known, precipitation of titanium hydroxide
from sulfate solutions leads to the formation of anatase form
irrespective of pH liquor solution.

As a result of the performed experiments it was found that
when precipitating fit hydroxide by method of gradual
addition of a precipitator a stable sol in quantity ~75% of
total hydroxide precipitator mass is formed in suspension
solution. Thus, even when the rate of precipitator addition
decreases by 1000 times a considerable part of titanium
hydroxide is formed not on the surface of rutile particles but
in the volume of the solution. In our opinion, obtained results
can be explained by the fact that in contrast to mechanism of
ion crystal nuclei formation, heterogeneous and
homogeneous formation of titanium hydroxide and other
d-metals follows the same mechanism. The essence of the
latter is the growth of polymeric chain of polynuclear
hydroxo-complexes. That is why probability of
heterogeneous and homogenous precipitation of hydroxides
is the same and therefore the processes proceed at practically
equal rate.

It should be noted, that independently of the precipitator
addition rate in reaction zone (i.e. on the boundary of
ammonia solution drop contact with the titanium salt
solution) high degree of solution supersaturation takes place.
For example, in studied experimental conditions
concentration of OH- ions changes from 2 to 10–12 mol/l
and of TiO$^{2+}$ from 0.06 to 10–5 mol/l. Therefore, hydroxide precipitation proceeds very quickly and the relation of hydroxide amounts precipitated heterogeneously and homogenously is determined by the volume of reaction zone and rutile particles content in it rather than by precipitation rate. Precipitating hydroxide by method of appearing reactants shows that the change of supersaturation degree in reaction zone will be considerably smaller. For example, when using urea hydrolysis concentration of hydroxide-ions (at pH change of mother liquor from 0 to 2 units) changes only by 100 times. This decrease in the degree of mother liquor precipitation results in abrupt decreasing of hydroxide precipitation rate, and, therefore, should cause formation of monodisperse particles. This conclusion was verified by experiment by the authors [9], who had determined that at fit hydroxide precipitation, almost spherical particles with the size of ~ 2 μ were formed by aggregating of primary anatase nanoparticles (size 4 - 5 nm). The authors [10] found that up to 500-fold excess of urea the hydroxide precipitation proceeds predominantly in heterogeneous manner (for the experiments plates of glass, polyethylene and polypropylene were employed).

It was also found that at further rise of urea content homogenous precipitation predominated. Besides, fit hydroxide precipitates in a form of anatase and only at decrease of urea excess by less than 150 times precipitate of titanium hydroxide may be formed as the mixture of both crystal structures – rutile and anatase ones.

Therefore, in the experiments carried out in our studies, 250-fold excess of urea in ratio to initial content of titanium was used. Urea hydrolysis was initiated by heating solutions up to 70°C. Precipitation was performed at continuous stirring of the suspension. The process was caused when mother liquor acidity reached pH = 2.0. It was assumed that in the case when coagulation-stable sol of hydroxide is formed, the sol can be easily separated from the composite precipitate by washing or filtering.

The results of the experiments have shown, that at titanium hydroxide precipitation by urea, TiO(OH)$_2$ sol is not practically formed. Under the given experimental conditions urea is likely to decompose on rutile particles surfaces thus giving rise to alkalifying solution at oxide particles surface and initiating polymerization of titanium hydroxo-complexes $[(TiO)_{x}(OH)_{2x+}]^x$. Since the rate of polymerization is much higher than diffusion rate of polynuclear hydroxo-complexes being formed in the solution volume, greater part of critical nuclei of fit hydroxide remains bound to rutile surface.

To confirm the possibility of catalytic action of rutile on urea hydrolysis we compared the rate of acidity change of urea solution at constant temperature both in presence and absence of TiO$_2$ suspension (Fig.2).

It was determined, that in such equal conditions (i.e. initial acidity of solutions, urea concentration, temperature, heating rate and rate of solution stirring) in presence of rutile the rate of urea hydrolysis is noticeably higher. Was assumed that urea is adsorbed on TiO$_2$ surface, for example, by H-bonds between its NH$_2$-groups and hydroxyl groups of titanium oxide. As a result of adsorption the strength of bonds between nitrogen atoms and those of carbon in CO(NH$_2$)$_2$ molecule can decrease thus diminishing activation energy of hydrolysis. Therefore, possibility of rutile-anatase composite synthesis by the method combining processes of heterogeneous nucleation and gradual accumulation of the precipitator is determined by the ability of the reagent chosen to decompose just in the reaction zone (i.e. on the surface of rutile microparticles) rather than by the precipitation rate and the degree of supersaturation in the reaction zone.

To determine the time for polymerization of titanium oxyhydroxide precipitate to be completed we have studied the dynamics of mother liquor acidity changes. In Fig.3 typical kinetic curves of solution acidity change over the precipitate of fresh-precipitated titanium hydroxide are shown.

It was found that after addition of NH$_4$OH solution the acidity of suspension continues to decrease quickly and only
in ~2.5 min the rate of its change diminishes rapidly. Then, on kinetic curves pH exponentially increases during ~120 min. In our opinion, the first stage of solution acidity change can be explained by slow equalization of precipitator concentration in the solution volume, since oxyhydroxide particles are quickly formed on the boundary of TiOCl₂ and NH₄OH solutions contact. Exponential growth of pH during next 2 hours is consistently explained by ions OH⁻ releasing with the formation of intraparticle olative (bridged) bonds between neighboring titanium cations 1:

\[ 2 \equiv \text{Ti-OH} \rightarrow =\text{Ti(OH)Ti} = + \text{OH}^- . \]

Thus, investigation of mother liquors acidity at ageing of titanium hydroxide has shown that in 2 hours the main fraction of OH-groups accessible for interaction is transformed into olative bonds. We can expect that hydroxide particle aggregates acquire extra rigidity and with further intraparticle polymerization of gel they can keep their structure.

### 3.3. Standardizing Parameters of Rutile-Anatase Composite Washing, Drying and Calcinations.

Precipitating rutile-anatase composite from mother liquor without breaking hydroxide “superstructure” on the surface of rutile particles is rather complex task. Suspension filtering or centrifuging leads to packing of obtained deposits. This tends to particles aggregation as a result of initiated processes of olation and oxalation. As a result of hydroxide precipitate washing by water in accordance with the acid-salt concentration ratio, in mother liquor the processes of the precipitate coagulative aggregation and peptization can be initiated. Therefore, we used 0.01 M solution of hydrochloric acid as washing liquid. This permitted to remove ions of ammonium sulfate from the solution and to maintain the charge on hydroxide surface constant. Chloride-ions were removed by washing the precipitate with organic solvent. At washing decantation method was used: solution over the precipitate was drawn off with siphon, then a small amount of 0.01M solution of hydrochloric acid was added, the suspension was stirred and the operation was repeated up to the complete suspension washing off ammonium sulfate impurities. Similar method was used for washing the precipitate by polar organic solvents – isopropyl and amyl alcohols. Using isopropanol allows to extract quickly a great amount of water from the precipitate as well as to wash precipitator from chloride-ion impurity. The subsequent substitution of isopropanol with pentanol was done to prevent hydroxide particles aggregation at its drying because the high boiling temperature of amyl alcohol makes water azeotropic distillation possible [11].

To choose the conditions for oxide-hydroxide composite transformation into its oxide rutile-anatase form DTA-DSC and XRD studies were performed. It was found that complete dehydration of oxide-hydroxide composite occurs at temperature 180-200°C (DTA curve shows relatively high endothermal peak). Such high temperature is explained by removing coordination-bound water and dehydroxylation of titanium hydroxide. At further heating we can observe small exothermal peak at 410-430°C which is evidence of X-ray amorphous oxyhydroxide transformation into anatase crystalline form.

Thus, drying was performed in two steps keeping composite precipitate for one hour at temperature 135°C (boiling in amyl alcohol for removing coordination-bound water) and at temperature 200°C (to remove alcohol traces and to get complete dehydration of the composite). In order to increase titanium oxyhydroxide degree of crystallinity the samples of composite was calcinated at 300, 400, 600 and 800°C for 3 hours. It should be noted, that together with oxyhydroxide dehydration the nature of its bond with rutile surface as bridges =Ti(OH)Ti= as well as H-bonds between OH-groups in the point of anatase and rutile particles contact are able to dehydrate and to be transformed into stronger o xo-bonds. At further composite calcinations structural change of particles “contact points” takes place, the former leads to ordering and increasing the number of o xo-bonds between rutile phase and that of anatase.

![Figure 4. XRD profiles for rutile-substrate (1) and rutile-anatase composite (2) after calcination at 600°C for 3 hours. (A – anatase diffraction peak).](Image)
anatase phase took place between 400 and 600°C (Fig.4, curve 2).

Electron microscopy studies of obtained composites did not allow us to identify an individual phase of anatase at rutile surface. Therefore, for identification of particles “superstructure” the sedimentation of the titanium hydroxide on the surface of rutile particles was carried with at presence of zirconium(IV) ions which was used as a probe.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.

Electron microscopy studies of obtained composites did not allow us to identify an individual phase of anatase at rutile surface. Therefore, for identification of particles “superstructure” the sedimentation of the titanium hydroxide on the surface of rutile particles was carried with at presence of zirconium(IV) ions which was used as a probe.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.

Coprecipitation of titanium and zirconium hydroxides, was carried from a solution containing 0.6 M TiOCl₂ and 0.1 M ZrOCl₂. According to calculations of solubility’s appropriate hydroxides, at such concentrations precipitation TiO(OH)₂ begins at pH 0.6, and Zr(OH)₄⁻ at pH 1.9. Since the deposition was performed at pH 2.5, the precipitate contained a mixture of the both hydroxides.
Rutile-anatase Composite Catalyst Formed by Coupling Anatase and Rutile Particles

Figure 6. Dependence of formaldehyde concentration (1), formic acid (2,3) and carbon dioxide (4) on residence reaction time of photooxidation at rutile-anatase composite calcinated at 600°C for 3 hours. Curve (2) depicts the calculation results of adsorbed formic acid.

The content of formaldehyde in a gas stream at different temperatures was determined for definition of limiting stage of process rate. It was found that in a temperature range 293÷323 K oxidation process proceeds in a kinetic mode. For all examined oxides the obtained rate constants of photoinduced oxidation of formaldehyde are well linearized on the coordinates of Arrhenius equation in this temperature range with the apparent activation energy 6÷25 kJ/mol. In Fig.6 the dependences between apparent activation energies of photoinduced oxidation of formaldehyde to formic acid and calcination temperatures of titanium dioxide and composite (10% anatase + 90% rutile) are shown.

According to data of Fig.7, crystalline structures of titanium dioxide play an important role in the formaldehyde photoinduced oxidation rate. The oxidation of formaldehyde with the minimum activation energy is achieved at usage as catalyst a crystalline anatase obtained by calcination of titanium oxyhydroxide in temperature range 400-600°C (curve 1). At the same time, the partial oxidation of formaldehyde on rutile-anatase composite with 10-w.t.% content of crystalline anatase also is realized with the minimum activation energy equal to ~6 kJ/mol (the curve 2). So far as the 10% excess of crystalline anatase particles is deficient for complete covering of rutile surface that it is possible to draw a conclusion about synergism of photoinduced catalytic activity of two coupled crystalline structures of titanium dioxide. Apparently, that phase boundary of anatase and rutile promotes formation of new adsorptive centers on a surface of a composite material and favors the increase of concentration of photo-generated electrons and holes due to decrease of their recombination rate. Our experimental result implies that the mixed phase of anatase and rutile can markedly enhance the photocatalytic activity of titanium dioxide.

Figure 7. Dependence of apparent activation energies of photoinduced oxidation of formaldehyde to formic acid on calcination temperatures of titanium dioxides (1) and 10% rutile-anatase composite (2). (All samples of titanium dioxide and composite were subjected to calcinations for 3 hours).

3. Conclusion

Thus, the way of synthesis of the rutile-anatase composite catalyst is developed by deposition of the titanium(IV) oxyhydroxide on a surface of rutile particles with the subsequent it dehydration and calcination for formation of an anatase crystal phase. To obtain composites with reproductive physico-chemical properties during synthesizing special attention was paid to control of its basic parameters. Concentrations of metal ions, hydrogen and rutile particles, the degree of mother liquor supersaturation, the tome of hydroxide ageing, temperature and time of composite drying and calcination were considered as above mentioned parameters.

Investigations of formaldehyde photoinduced oxidation on modified by anatase particles rutile has shown its great activity which can be evidence that there exists synergism of photoinduced catalytic activity of two coupled crystal structures of titanium dioxide. The modification of rutile surface by particles of another semiconductor can be used as a perspective way of the designing of new improved photocatalytic systems.

REFERENCES

[1] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann. Environmental applications of semiconductor photocatalysis, Chemical Reviews, Vol. 95, 69-96, 1995.

[2] O. Carp, C.L. Huisman, A. Reller. Photoinduced reactivity of titanium dioxide, Progress in Solid State Chemistry, Vol. 32, 33-177, 2004.

[3] K. Lu, J. Yu, K. Deng, X. Li, M. Li. Effect of phase
structures on the formation rate of hydroxyl radicals on the surface of TiO2. J. Phys. Chem. Solids, Vol. 71, No 4, 519-522, 2010.

[4] J. Xu, W. Wang, S. Sun, L. Wang. Enhancing visible-light-induced photocatalytic activity by coupling with wide-band-gap semiconductor: A case study on Bi2WO6/TiO2. Applied Catalysis B: Environmental, Vol. 111, 126-132, 2012.

[5] A. Nikolenko, B. Melnykov. Photocatalytic Oxidation of Formaldehyde Vapour Using Amorphous Titanium Dioxide. Chem. & Chem. Techn., Vol. 4, 311-315, 2010.

[6] M. Graetzel, F. Rotzinger P. Raman spectroscopic evidence for the existence of titanyl (TiO^2+) in acidic aqueous solutions. Inorg. Chem., Vol. 24, 2320–2321, 1985.

[7] H. Einage, Y. Komatsu. Hydrolytic precipitation reaction of titanium(IV) from (Na, H)Cl aqueous solution. J. Inorg. Nucl. Chem. Vol. 43, 2443-2448, 1981.

[8] A. Tsevis, N. Spanos, P.G. Koutsoukos, A.J. Linde, J. Lyklem. Preparation and characterization of anatase powders, J. Chem. Soc., Faraday Trans., Vol. 94, 295-300, 1998.

[9] J. Subrt, V. Stengel, S. Bakardjieva, L. Szatmary. Synthesis of spherical metal oxide particles using homogeneous precipitation of aqueous solutions of metal sulfates with urea. Powder Technology, Vol. 169, 33-40, 2006.

[10] S. Yamabi, H. Imai. Synthesis of rutile and anatase films with high surface areas in aqueous solutions containing urea. Thin Solid Films, Vol. 434, 86-93, 2003.

[11] В.Г. Верещак, М.В. Никolenко, А.М. Калащенкова. Одержання малоагрегованих оксидних порошків, ВХХТ, 2013, Vol. 3, 53-58.

[12] B. Huang, S. Saka. Photocatalytic activity of TiO2 crystallite activated carbon composites prepared in supercritical isopropanol for the decomposition of formaldehyde. J. Wood Sci., Vol. 49, 79-85, 2003.

[13] X. Xiao, D. Liao, H. Zhang. Synthesis of TiO2 nano-particles and their photocatalytic activity for formaldehyde and methyl orange degradation. Front. Chem. Eng. China. Vol.1(2), 178-183, 2007.

[14] Y. Qing, G. Fen, X. Ying, X. Cai-jun, G. Bao-wen. Фотокаталитическая деструкция формальдегида на пористой пленке из TiO2. Huanjing kexue, Vol. 26, No 4, 35-39, 2005.

[15] Y. Jian-Jun, L. Dong-Xu, L. Qing-Lin, Z. Zhi-Jun, W. Han-Qing. Mechanism of Photocatalytic Oxidation of Formaldehyde. J. Acta Phys. Chim. Sin., Vol. 17, No 3, 278-281, 2001.

[16] S. Song, D. Jianjun, B. Jun, G. Chen, Q. Zeming. Photocatalytic Oxidation of Gaseous Formaldehyde on TiO2: An In Situ DRIFTS Study. Catal. Lett., Vol. 137, 239–246, 2010.

[17] C. Zhang, H. He, K. Tanaka. Catalytic performance and mechanism of a Pt/TiO2 catalyst for the oxidation of formaldehyde at room temperature. Appl. Catal. B, Environ., Vol. 65, 3743, 2006.

[18] J.L. Shie, C.H. Lee, C.S. Chiou, C.T. Chang, C.C. Chang, C.Y. Chang. Photodegradation kinetics of formaldehyde using light sources of UVA, UVC and UVLED in the presence of composed silver titanium oxide photocatalyst. J. Hazard. Mater., Vol. 155, No1-2, 164-172, 2008.