

THE INFLUENCE OF MO, CO, AND V ON THE PROPERTIES OF THE PHOTOCATALYSTS TYPE TiO₂/Al₂O₃

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Summary. The paper presents a study on the impact of dopant Mo, Co and V on the physico-chemical properties and photocatalytic TiO₂/Al₂O₃ a contact base. Activity of the catalysts obtained were tested in the reaction of the total oxidation of phenol in the photocatalytic oxidation processes and advanced oxidation with hydrogen peroxide. Observed a positive effect of hydrogen peroxide on the photo-oxidation reaction of phenol on the catalyst Co-TiO₂/Al₂O₃.

Key words: advanced oxidation processes, titanium catalysts, promoters, photocatalysis

INTRODUCTION

There are numerous, very dangerous, organic water pollutants such as aldehydes, chlorobenzenes, plasticizers, organotin compounds, pesticides, acrylamides or complexones (EDTA, NTA). When a process of water purification is considered, phenols are among the most persistent pollutants, which is a result of their high stability and perfect water solubility. In a process of chlorination of water containing these compounds, toxic chlorophenols are formed, giving water an unpleasant odour. Among many standard methods of removing organic substances from water such as coagulation, flotation, chemical oxidation or sorption processes, technologies utilizing photocatalytic processes are the most effective. Little costs as well as lack of negative influence on natural environment are additional advantages of photocatalytic processes. However, AOP technique is not disadvantages free. Its major flaws are: necessity of separation of catalyst phase from liquid (there are not any effective methods of catalyst immobilization on a reactor bed), long time of contact in case of degradation of complex organic compounds. The goal of this paper was investigation of influence of electron promoters such as Mo, Co and V on activity of TiO₂ photocatalysts based on an anatase form in order to obtain increased activity of catalysts.

EXPERIMENTAL PROCEDURE

Materials and reagents

Titanium catalysts and titanium doped with metals catalysts were based on a carrier γ - Al_2O_3 which total surface area was $80.4 \text{ m}^2 \text{ g}^{-1}$ – Peschiney (France) All reagents used for the purpose of the investigation including: TiCl_4 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{H}_2\text{Na}_2\text{EDTA}$, 25% water solution of ammonia, $(\text{NH}_4)_6 \cdot \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, V_2O_5 , H_2O_2 30%, H_2SO_4 , Ag_2SO_4 , $\text{C}_{36}\text{H}_{24}\text{FeN}_6\text{O}_4\text{S}$ (indicator), $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, HgSO_4 , were analytically pure, gaseous oxygen - bottle (99,995%) – Praxair, gaseous nitrogen (bottle) (99,995%) – Praxair.

Preparation of catalysts

In order to prepare catalysts $\text{TiO}_2/\text{Al}_2\text{O}_3$, and series $\text{Co-TiO}_2/\text{Al}_2\text{O}_3$, $\text{Mo-TiO}_2/\text{Al}_2\text{O}_3$ and $\text{V-TiO}_2/\text{Al}_2\text{O}_3$ a double impregnation method (DIM) was utilised, with a modification of a carrier with a complexing compound, as described in the work [Barcicki *et al.* 1981]. DIM method uses disodium salt of ethylenediaminetetraacetic acid $\text{H}_2\text{Na}_2\text{EDTA}$ as a complexing agent, what favours obtaining high dispersion of metallic phase and enables formation of increased activity systems. Base catalysts $\text{TiO}_2/\text{Al}_2\text{O}_3$ were obtained as follows: impregnation of Al_2O_3 carrier by means of 0.1M solution of $\text{H}_2\text{Na}_2\text{EDTA}$ at temperature of 343K, for 30 minutes, filtering off and drying the carrier for 1 hour at temperature of 388K in an atmosphere of air followed by impregnation of activated preparation with 10% solution of TiCl_4 for 3 and 6 minutes respectively, separation of precursors from water phase, than drying at 388K for 1 hour and finally calcination at temperature of 873K for 3 hours. Systems of Co, Mo and V were obtained through introduction of a promoter by means of DIM method so that during the first stage proper catalyst $\text{TiO}_2/\text{Al}_2\text{O}_3$ had been impregnated for 30 minutes with 0.1M solution of $\text{H}_2\text{Na}_2\text{EDTA}$ at temperature of 343K and than the system was filtered off and dried for 1 hour at 388K. The second stage of the impregnation, which had been carried out for 10 minutes, included impregnation with 2.5% ammonia solution of $\text{Co}(\text{NO}_3)_2$ at room temperature, than impregnation with 5% ammonia molybdate solution and finally impregnation with basic solution of V_2O_5 (2.3 g NaOH per 1 g V_2O_5). Obtained precursors of catalysts were dried at 388K and than, for 3 hours, they were subjected to calcination in an atmosphere of air at temperature of 873K. In order to determine content of metals being an active phase of catalysts $\text{Mo-TiO}_2/\text{Al}_2\text{O}_3$, $\text{Co-TiO}_2/\text{Al}_2\text{O}_3$ – Ti, Mo and Co, method of X-ray fluorescence (XRF), based on K_α peak, was used and performed by means of apparatus made by Canberra company, [Alloway and Ayres 1999]. Determination of surface area of samples of the catalysts was based on BET method, which sets on measuring argon ad-

sorption at the temperature of liquid nitrogen, and was conducted by means of static volumetric analysers guaranteeing vacuum no lesser than $2 \cdot 10^{-6}$ kPa [Ościk 1973]. Analysis of fractional composition of Co, Mo and V catalysts was conducted by means of X-ray diffraction method (XRD) [Ziółek and Nowak 1999]. CuK radiation was utilised and DRON-2 diffractometer was used.

Equipment for measuring photocatalysts activity

For the purpose of measuring oxidation of organic pollutants in waste water, band reactor described in a paper [Czech and Nazimek 2004] was used. The reactor was designed from organic glass transparent and resistant to UV light. Inside the reactor two tubes were placed above the UV lamp (254 nm, 50 Hz). The intensity of the UV lamp was measured by the VLX254 meter being a product of Vilber Lourmat company. Mixture of oxygen and nitrogen (air) necessary for the process of photooxidation was composed of oxygen and nitrogen from the bottles, by means of mass controllers made by BetaErg company.

Method of conducting measurements

Sample of waste water, characterising with standard COD (chemical oxygen demand) $3000 \text{ mg O}_2 \text{ dm}^{-3}$, which is a value close to these noted in case of actual sewage and at the same time exceeding values permitted by norms, which itself is an indicator (in respect to COD), of significant concentration of sewage, was introduced into the reactor, after rotation of a band mixer was started. Than, through inspection openings in the reactor, known mass of the investigated catalyst was added. The measurements consisted in forcing 500 cm^3 of investigated waste water, together with a fed mixture of gases O_2 and N_2 (21% oxygen and 79% nitrogen, $V = 24 \text{ dm}^3 \text{ h}^{-1}$), through a moving catalytic assembly being a closed loop, with a constant space velocity of $4000 \text{ cm}^3 \text{ h}^{-1}$. The sample of sewage for the investigation of COD was retrieved after an intended investigated time (however, not sooner than after 7.5 minutes) after the reactor had been completely emptied. The measurements were conducted at room temperature.

Determination of organic compounds concentration in water

Content of organic compounds, before samples were treated and after the process of catalysis, were assessed trough evaluation of COD determined by means of known dichromate method. The methodology of measuring COD was analogous to one described in the work [Czech and Nazimek 2004].

Degree of COD reduction was calculated using formula (1):

$$X = [(\text{COD}_{\text{introduced}} - \text{COD}_{\text{obtained}}) / \text{COD}_{\text{introduced}}] \cdot 100\% \quad (1)$$

where COD – chemical oxygen demand in $\text{mg O}_2 \text{ dm}^{-3}$

RESULTS AND DISCUSSIONS

Physical-chemical properties of obtained objects

In table 1, results of physical-chemical analyses of obtained samples of titanium catalysts promoted with different metals by means of DIM method were listed.

Table 1. Physical and chemical properties of the obtained catalysts

Catalyst	Content of Ti % w/w	Content of promoter % w/w	Total surface area $\text{m}^2 \text{g}^{-1}$
ATiO ₂	2.97	-	78.6
BTiO ₂	5.82	-	77.9
Mo-TiO ₂	5.82	3.11	69.8
Co-TiO ₂	5.82	1.14	72.3
V-TiO ₂	5.82	5.12	60.2

After, introducing a promoter, additional process of impregnation by means of DIM method had been carried out, total surface area of obtained preparations changed, and ranged from 60.2 to 72.3 $\text{m}^2 \text{g}^{-1}$. The second value of the total surface area, and at the same time the lowest concentration of metal – the promoter, was observed in case of titanium catalyst promoted with cobalt.

Photocatalytic oxidation of phenol

In the figure1, dependence of degree of COD reduction, being a derivative of phenol presence, on time of process duration on catalysts ATiO₂ and BTiO₂ was presented.

In both cases high level of reduction of COD derived from phenol was observed, but it should be noted that increase of TiO₂ in the catalyst did not significantly influenced increase of COD reduction degree, and it certainly was not a proportional dependence. The lack of proportionality suggests that in case of investigated conditions of the photooxidation process, diffusion processes are the factor limiting rate of phenol reduction. These are probably processes of inner diffusion in pores of the catalyst, as it takes place in other heterogeneous catalytic processes [Nazimek *et al.* 2006]. In the figure 2 changes in the reduction of COD derived from phenol on titanium catalysts, based on the system BTiO₂ and doped with Mo, Co, and V were presented.

Introduction of metal dope to a base catalyst has changed image of the process of phenol photooxidation. Characteristic maximum and minimum of reduction degree of phenol content were observed, which was particularly clearly no-

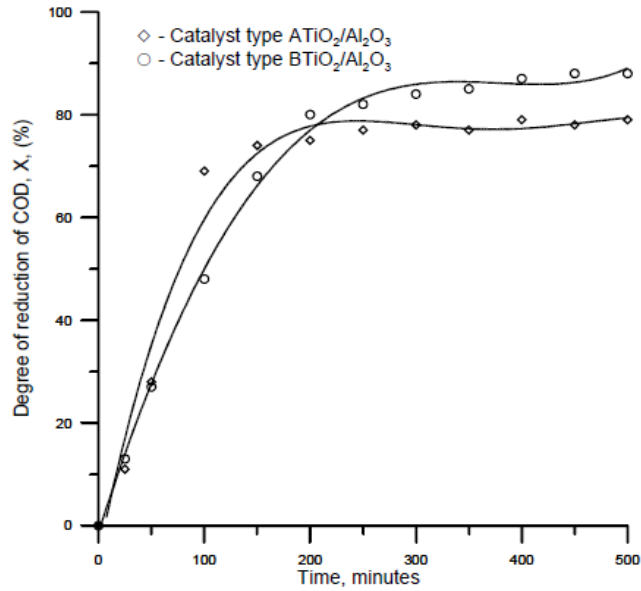


Fig. 1. Changes in the reduction of COD derived from phenol and catalyst ATiO₂ (2.97% wght. TiO₂) BTiO₂ (5.82% wght. TiO₂) as a function of the duration of the measurement

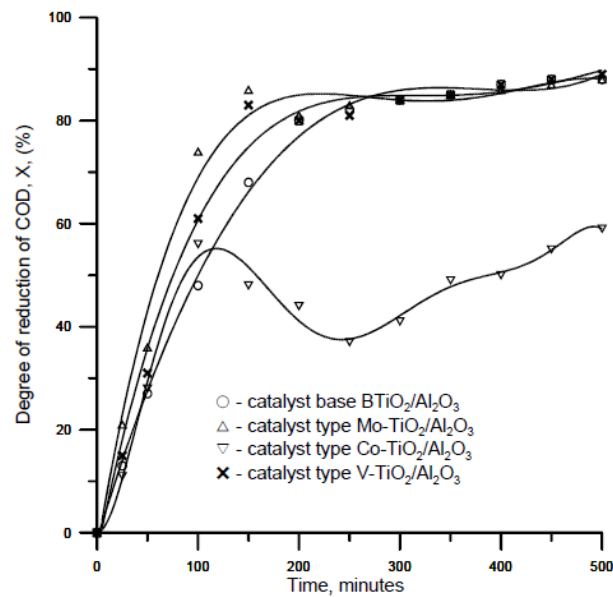


Fig. 2. Changes in the reduction of COD derived from phenol titanium catalysts, based on the system BTiO₂ (5.82% wght. TiO₂) doped Mo, Co, and V

noticeable in case of catalyst doped with cobalt. Clear improvement of catalytic properties was noted only in case of catalyst doped with vanadium. Observed changes can be interpreted in many ways, however, the fact of occurrence of maximum and minimum of reduction degree and than increase of this value during the course of the process seems to suggest presence of a mechanism of self-contamination of catalyst's surface, as observed in some reactions in which hydrogen and carbohydrates take part [Nazimek and Ryczkowski 1989], and than slow process of decontamination under the influence of oxygen.

Advanced oxidation of sewage with hydrogen peroxide (AOPs)

0.5 cm³ H₂O₂ (30%) was introduced into 500 cm³ of sewage, characterising with COD 3000 mg O₂ dm⁻³, and than a measurement of changes of COD reduction degree in the function of time, as described above, was carried out. Obtained results for a measuring time of 500 minutes (final values) were listed in table 2.

Table 2. Changes in the reduction of COD derived from phenol advanced oxidation conditions

Type of catalyst	Conditions of the process course	
	without of H ₂ O ₂	in presence of H ₂ O ₂
ATiO ₂	79	77
BTiO ₂	88	92
Mo-TiO ₂	88	77
Co-TiO ₂	59	91
V-TiO ₂	89	98

Only in case of catalyst promoted with cobalt significant increase of COD reduction from, 59% to 91%, was noted. Therefore, presence of atomic oxygen originating from decomposition of hydrogen peroxide cancelled the process of self-contamination of active surface of the contact. Positive effect of hydrogen peroxide was noted also in case of catalyst promoted with vanadium (9% increase of reduction degree).

CONCLUSIONS

Catalysts TiO₂/Al₂O₃ characterise with high efficiency in degradation of phenol present in sewage. The highest reduction of COD was observed during oxidation carried out in presence of BTiO₂ catalyst supported on γ -Al₂O₃ carrier. Satisfying reduction of about 77% is obtained when catalyst with lower content of TiO₂ is used. Carried out research of phenol degradation on systems of Co, Mo and V showed that way in which promoters affect degradation vary. It was

especially visible in case of cobalt when a process of self-contamination occurred. Introduction of H_2O_2 into the process definitely changed the course of phenol photooxidation. Presence of atomic oxygen on a surface of photocatalyst promoted with cobalt caused rapid increase of COD reduction degree, what suggests elimination of self-contamination process from the active surface. Comparing results obtained for catalysts TiO_2/Al_2O_3 , characterising with different content of titanium dioxide, it can be concluded that semiconductors having lower content of TiO_2 are not sensitive to oxidizer addition. Investigated systems characterise with lower or slightly higher, reaching couple percent, efficiency of phenol degradation (except for catalyst with cobalt addition) with addition of H_2O_2 when compared to TiO_2/Al_2O_3 . Therefore, it can be concluded that photocatalytic oxidation of phenol progresses mainly with participation of TiO_2 .

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WPLYW DODATKU MO, CO ORAZ V NA WŁAŚCIWOŚCI FOTOKATALIZATORÓW TiO_2/Al_2O_3

Streszczenie. W pracy przedstawiono badania wpływu domieszki Mo, Co oraz V na właściwości fizykochemiczne oraz fotokatalityczne bazowych kontaktów typu TiO_2/Al_2O_3 . Właściwości katalityczne otrzymanych kontaktów badano w reakcji fotoutleniania fenolu, a także w procesie pogłębionego fotoutleniania tego związku z udziałem nadtlenku wodoru. Zauważono wyraźny, pozytywny wpływ nadtlenku wodoru na przebieg reakcji fotoutleniania fenolu na katalizatorze Co- TiO_2/Al_2O_3 .

Słowa kluczowe: zaawansowane procesy utleniania, katalizatory tytanowe, promotory, fotokataliza