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PHOTOCATALYTIC OXIDATION OF FORMALDEHYDE VAPOUR USING AMORPHOUS TITANIUM DIOXIDE

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Abstract. The gas-phase photocatalytic oxidation of formaldehyde over illuminated amorphous titanium dioxide was investigated using a model flow reactor with the following experimental conditions: 0.1–0.5 l/min flow rate and an organic compound concentration range of 0.006–0.082 mol/m³. Mathematical model of the process which includes two sequential stages: formation of formic acid and its subsequent oxidation to CO₂ was offered. It was found that when the amount of TiO₂ on carrying agent (anodized titanium) is 3.6 mg/cm², the intensity of UV lamp is 18 W and the catalyst temperature is 293 K, values of observed rate constants are equal to 6.5·10⁻³ s⁻¹ for the first stage and 1·10⁻² s⁻¹ for the second stage of oxidation. The apparent activation energy of photocatalytic oxidation process of formaldehyde vapour for temperature interval 293–323 K is 20.2 kJ/mol.

Keywords: titanium dioxide, formaldehyde, photocatalytic oxidation process, model flow reactor.

1. Introduction

At present to purify gas emission the processes of absorption, adsorption, condensation, membrane separation as well as methods of thermal, chemical, catalytic and biochemical purification are used. It is possible to extend capabilities of the above methods of gas emission purification from toxic organic substances using the process of photocatalytic oxidation [1] which offers complete mineralization of organic compounds. Photocatalytic oxidation comprises the employment of semiconducting materials able to absorb light and generates radical particles with high oxidizing capacity. Gas-phase heterogeneous photocatalysis using TiO₂ was first explored in 1990 [2]. It was reported about high levels of destruction of trichloroethylene when TiO₂ was irradiated with ultraviolet light. Since then, series of other organic compounds photodegradation in the gas-phase has been extensively investigated [3, 4].

In this paper, the mechanism of photocatalytic oxidation of formaldehyde in a model flow reactor is studied. Formaldehyde is known to be a widespread organic air pollutant with relatively low maximum permissible concentration. For example, in the room air maximum permissible concentration of formaldehyde is 0.5 mg/m³. At present investigations into photocatalytic oxidation of formaldehyde were carried out by several authors [5-7]. The authors [5] show the possibility of rapid photodestruction of formaldehyde on dioxide titanium catalyst containing admixtures of carbon as an activator. Nanodispersible dioxide of titanium was used as a catalyst in [6]. It was concluded that the catalyst involved appears to be more active and promising for technical application. In work [7] photooxidation of formaldehyde in gas flow on titanium dioxide made in a form of a thin porous film on the surface of stainless steel gauze was studied. Unfortunately, the data submitted in [5-7] don't allow estimating efficiency of using photocatalysis for purifying industrial gas emissions.

The point is that designing of photoreactors needs thorough investigations into oxidation process at model or pilot plants of a flow type. Therefore, we seek to investigate kinetics of formaldehyde destruction in a model flow reactor. This data will be necessary for calculation of a reactor volume according to the initial concentration of formaldehyde and for determining conditions to reach complete transformation of formaldehyde to CO₂.

2. Experimental

Investigations were carried out in a model plant, its main part being flow photoreactor. The UV lamp TLD18 W/08 class UVA, capacity 18 W and maximum emission band 370 nm was located axially in the reactor. The reactor length is 500 mm and reaction zone volume is 530 ml.

Amorphous titanium dioxide obtained from titanium hydroxide was used as a catalyst. Titanium hydroxide has

been prepared by precipitation at 298 K and pH = 11.0 in a stirred reactor by mixing TiOSO_4 and ammonium hydroxide so as to keep solution supersaturation constant throughout the precipitation process [8]: $\text{TiO}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{TiO}(\text{OH})_2(\text{s})$. Then precipitate was filtered, extensively washed and calcined at 450 K. The amorphous structure of the oxide was confirmed by X-ray diffraction analysis.

Aqueous suspension of obtained TiO_2 powder was applied on the inner part of titanium pipe with the diameter of 50 mm and surface area 700 cm^2 . The precipitate obtained was dried at 383 K. The amount of TiO_2 on the carrier surface made up 3.6 mg/cm^2 .

To obtain a formaldehyde vapour the air current passed over 37 % solution of formaldehyde with a certain rate (0.1–0.5 l/min). In a mixing flask the formaldehyde vapour was mixed with dried air and then entered the reactor. The temperature of the catalyst surface (293–400 K) was changed by means of cooling or heating the surface of the reactor case. When analyzing the gas mixture, the content of formaldehyde, formic acid and CO_2 was determined. Formaldehyde content was determined by a photometric method employing colour reaction with phenylhydrazine. Formic acid was reduced in HCl medium by means of metallic magnesium with subsequent photometric determination of reduction product, *i.e.* formaldehyde. CO_2 content was found by potentiometric back titration.

3. Results and Discussion

Before starting the investigation to obtain a stationary state of mass and heat exchange the reactor was in operating conditions for an hour. In previous studies it was determined that when UV-irradiation or TiO_2 -catalyst was absent, the oxidation of formaldehyde did not proceed even at elevated temperature up to 320 K. At the same time similar experiments at 400 K showed that as a result of auto-oxidation the concentration of formaldehyde vapours can slightly decrease (up to 5 % in a studied time range). When exposed to the light of UV lamp photocatalyst showed natural reduction of final concentration of formaldehyde. After determining the composition of the gas mixture at various reactor loads it was found that with the decrease of the reaction mixture flow rate through the reactor concentration of formaldehyde reduces gradually, CO_2 concentration gradually increases and the amount of formic acid first slightly increases and then reduces practically to zero (as to possibilities to use procedure of photometric determination). The example of graphic representation of relationship between concentration of all the determined components of the reaction mixture and reference time of photocatalytic oxidation reaction is shown in Fig.1. Reference time of the reaction was calculated as the relationship between the volume of reactor

reaction zone and the value of its loading [8]. The value of reference time τ_0 at which the concentration of formaldehyde in the reactor accounted for its initial concentration measured in no UV radiation condition ($\Delta\tau = \tau - \tau_0$) was taken as a starting point.

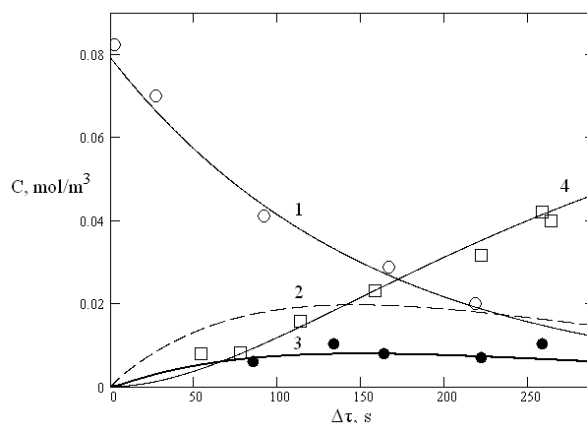


Fig.1. Dependence of formaldehyde concentration(1), formic acid (2, 3) and carbon dioxide (4) on conventional reaction time of photooxidation at catalyst temperature 293 K. (Dots show the experimental data and the curves are plotted on the basis of the mathematical model. The curve (2) depicts the calculation results of adsorbed formic acid)

Analysis of obtained kinetic data showed that the values of formaldehyde oxidation rate are linearized best of all in the coordinates of the first-order equation $\ln C - \Delta\tau$. To explain the regularity determined we should take into account that the kinetics of higher-order reactions can be levelled to the kinetics of lower order under the conditions when one of the reaction components has rather high concentration. Also the first-order kinetics follows from the known equation for a heterogeneous chemical process:

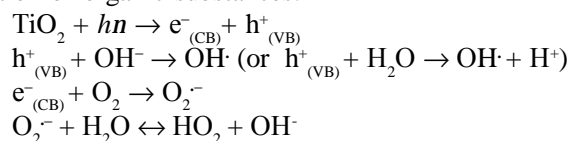
$$W_A^{HCOH} = \frac{C_{HCOH}^0}{\frac{1}{b_1 S} + \frac{1}{k_2 S C_{Ox}}} = K_A C_{HCOH}^0$$

where W_A^{HCOH} is the observed rate of formaldehyde oxidation; C_{HCOH}^0 is the concentration of formaldehyde in a gas phase; C_{Ox} is the concentration of oxidizer active particles; b is the mass exchange coefficient (relationship of a diffusion coefficient to the thickness of surface layer); k_2 is the constant of a reaction rate; S is the catalyst surface.

The concentration of oxygen in the gas phase being hundred times as much as the amount of formaldehyde and generation of radical particles under the influence of

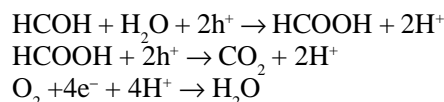
UV radiation occurring constantly, we can assume that concentration of radical particles does not practically change (at least in comparison with the concentration of formaldehyde). Therefore the coefficient of proportionality K_A can be assumed to be a stationary value, the values of and being invariable. Thus, photooxidation of formaldehyde under certain conditions can be described by the kinetic equation of the pseudofirst order.

As we know from [1], in absorbing light within the volume of TiO_2 particle a free electron and electronic vacancy are formed. The electron and the vacancy give rise to the formation of radical particles which cause oxidation of organic substances:



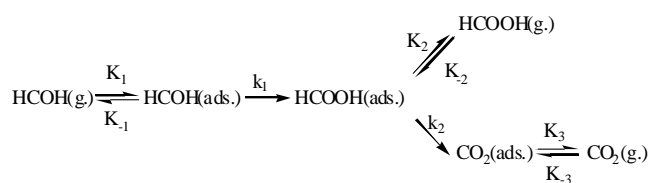
where $e^-_{(\text{CB})}$ is the electron of the conduction band, $h^+_{(\text{VB})}$ is the vacancy of valence band.

In general, oxidation-reduction processes on the surface of the semiconductor catalyst involving formaldehyde, formic acid and oxygen can be expressed as:



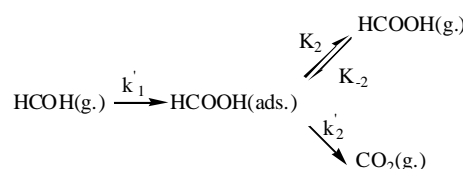
According to these reactions the kinetic scheme of a photocatalytic formaldehyde transformation should include, as a minimum, two sequential stages: the formation of the formic acid from formaldehyde followed by its oxidation to CO_2 . It is known that kinetics of heterogeneous processes is well described by the Langmuir-Hinshelwood model. In approximation of this model it is supposed that surface concentrations of reactants are in equilibrium as to their volume concentrations, and the molecules in the adsorbed layer appear to be very mobile. Before adsorbed they undergo numerous collisions. Under this assumption the adsorption equilibrium is described by the Langmuir isotherm and the reaction rate is determined by the law of surface action (analogous with the law of mass action for chemical processes proceeding on the solid surface).

In approximation of the Langmuir-Hinshelwood model formaldehyde oxidation on the catalyst surface should be regarded as the sequence of adsorption-desorption stages and chemical transformation:



where K_1 and K_{-1} are the constants of adsorption/desorption rate, k_1 is reaction constants, g is the gas phase, ads are the adsorbed particles.

Since in fact we know only the volume but not surface concentrations of components in a gas phase, the kinetic equation was presented in the form of rate-to-reagents concentration in a gas phase ratio. Therefore, to calculate rate constants a simplified model of the process was employed:



Mathematically such process is described by the following equations:

$$\begin{aligned} \frac{dC_{\text{HCOH(g.)}}}{dt} &= -k_1 C_{\text{HCOH(g.)}}; \\ \frac{dC_{\text{HCOOH(ads.)}}}{dt} &= k_1 C_{\text{HCOH(g.)}} - K_2 C_{\text{HCOOH(ads.)}} + K_{-2} C_{\text{HCOOH(g.)}} - k_2 C_{\text{HCOOH(ads.)}}; \\ \frac{dC_{\text{HCOOH(g.)}}}{dt} &= K_2 C_{\text{HCOOH(ads.)}} - K_{-2} C_{\text{HCOOH(g.)}}; \\ \frac{dC_{\text{CO}_2\text{(g.)}}}{dt} &= k_2 C_{\text{HCOOH(ads.)}}. \end{aligned}$$

$$\text{at } t = 0: C_{\text{HCOH}} = C_0,$$

$$C_{\text{HCOOH(ads.)}} = C_{\text{HCOOH(g.)}} = C_{\text{CO}_2\text{(ads.)}} = 0$$

When calculating the rate constants of the process investigated the model of a plug-flow reactor was used. Possibilities of using the model involved was experimentally proved by determining distribution function of the reagent residence time in a reactor. On the basis of experimental studies of response curves an average conversion of formaldehyde was calculated, in the plug-flow reactor it accounted for 63.8 % and in the model reactor it constituted 61.7 %. Closeness of the above values testifies that the process in the investigated model reactor can be considered as a plug flow [9]. We also made calculations of Reynolds number for the gas flow in the model reactor. It was found that in the investigated range of rates Reynolds number does not exceed 44 units. Such low value of Re number shows that under chosen experimental conditions the gas mixture flow is laminar. The opportunity of disturbing the laminar gas flow at the reactor outlet and inlet may be neglected as the length of the reactor exceeds its effective diameter by 20 fold.

Within the plug-flow model the concentrations of every reactant were determined (see Fig. 1). Calculations of the curves $C\Delta\tau$ were carried out by Runge-Kutt method with a fixed pitch of integration [9]. On the basis of experimental data and mathematical model the values of

constants k_1 and k_2 were calculated, the latter making up $6.5 \cdot 10^{-3} \text{ s}^{-1}$ and $1 \cdot 10^{-2} \text{ s}^{-1}$ respectively.

It was determined that the results of theoretical calculations agree with the experimental data provided the greater amount of formic acid is on the catalyst surface but not in the gas phase. This result is in accordance with the data of the authors [10], who found that when methanol undergoes photooxidation on TiO_2 catalyst the formiates which are collected on the oxide surface are being quickly formed. Besides, it should be mentioned that the results obtained can also be explained by the occurring process of formic acid oxidation to carbon oxide (II). To test this hypothesis we carried out additional investigations to reveal the presence of CO in the reaction mixture. This was done by means of determining the total amount of carbon when passing the gas mixture (at 673 K) through a pipe with an oxidized copper gauze which appears to be a catalyst of CO oxidation to CO_2 . The results of the experiments for the entire range of $\Delta\tau$ values showed no carbon oxide (II) in a gas outflow.

Thus, deviations of experimental data for the formic acid from calculated values should be explained by the increased adsorption on the catalyst surface. This conclusion is consistent with the literature data [11], which show that oxygencontaining organic substances may be selectively adsorbed on the oxides of titanium. In Fig. 1 the continuous line (curve 3) depicts the result of calculations for the amount of formic acid in the reactor gas phase with due account of its adsorption. The results of these calculations (given $K_1/K_2 = 10$) are in agreement with the experimental values obtained. Thus, the hypothesis of collecting formic acid molecules or ions on the catalyst surface explains the total set of experimental data.

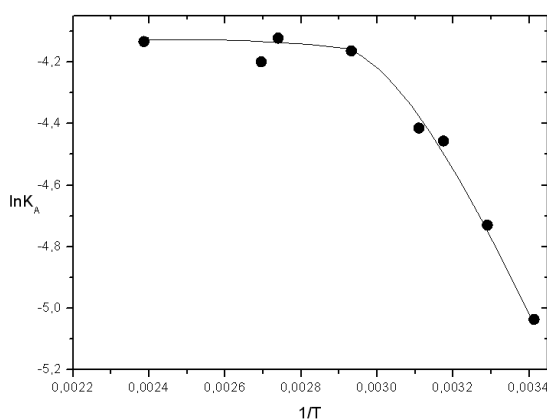


Fig. 2. Dependence between oxidation rate constants of formaldehyde and temperature of the catalyst in the coordinates of Arrhenius equation

The content of formaldehyde in the gas stream at different temperatures was determined for definition of limiting stage of the process rate. It was found that the

obtained rate constants are well linearized on the coordinates of Arrhenius equation in a temperature range of 293–323 K with the apparent activation energy 20.2 kJ/mol (see Fig. 2). Taking into account the low values of activation energies for radical reactions, it is possible to draw a conclusion that at room temperatures the oxidation process proceeds in a kinetic mode. As evident from Fig. 2, at temperatures higher 320 K the diffusive mode of oxidation process is observed.

4. Conclusions

On the basis of the investigations of formaldehyde destruction kinetics and collecting of formic acid and carbon (IV) in the gas medium of the reactor it was found that the rate of formaldehyde oxidation can be described by the kinetic equation of pseudofirst order. At modelling the photodestruction process by two sequential stages ($\text{HCHO} \rightarrow \text{HCOOH} \rightarrow \text{CO}_2$) it is necessary to assume that the formic acid is collected on the catalyst surface as the result of relatively strong adsorbability.

It was ascertained that under conditions of the flow reactor the observed rate constant of the formic acid photooxidation ($1 \cdot 10^{-2} \text{ s}^{-1}$) exceeds the corresponding value for formaldehyde ($6.5 \cdot 10^{-3} \text{ s}^{-1}$) only by 1.5 fold. Since this relationship of the values for rate constants of carboxylic acid and aldehyde oxidation may be caused by the difference both in diffusion coefficients and in rate constants of the chemical reactions themselves, it is impossible to explain differences in the rates of oxidation on the basis of the obtained experimental data.

The obtained results can be used for calculation of reactor volume according to initial concentration of formaldehyde and for determining conditions to reach complete transformation of formaldehyde to CO_2 . For example, under conditions of the model reactor at UV lamp power 18 W and 3.6 mg/cm^2 of TiO_2 on the surface being illuminated, practically complete purification of air containing 0.08 mol/m^3 of formaldehyde is achieved at $\tau \sim 450 \text{ s}$.

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ФОТОКАТАЛІТИЧНЕ ОКИСНЕННЯ ПАРІВ ФОРМАЛЬДЕГІДУ У ПРИСУТНОСТІ АМОРФНОГО ДІОКСИДУ ТИТАНУ

Анотація. Вивчено газофазне фотокаталітичне окиснення формальдегіду на опроміненому аморфному діоксиді титану, використовуючи модельний проточний реактор з наступними експериментальними умовами: $0.1-0.5 \text{ лжв}^{-1}$

швидкості потоку і концентрацією органічних сполук у діапазоні $0.006-0.082 \text{ моль/м}^3$. Запропонована математична модель процесу, яка включає дві послідовні стадії: утворення з формальдегіду метанової кислоти і її наступне окиснення до CO_2 . Знайдено, що при кількості TiO_2 на поверхні носія (анодованого титану) 3.6 мг/см^2 , потужності УФ-лампи класу UVA 18 Вт і температурі каталізатору 293 К величини умовних констант швидкості дорівнюють $6.5 \cdot 10^{-3} \text{ с}^{-1}$ для першої стадії і $1 \cdot 10^{-2} \text{ с}^{-1}$ для другої стадії окиснення. Ефективна енергія активації процесу фотокаталітичного окиснення парів формальдегіду у температурному інтервалі 293–323 К становила 20.2 кДж/моль.

Ключові слова: діоксид титану, формальдегід, фотокаталітичний окисний процес, модельний проточний реактор.