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Catalytic degradation of CH₂O and C₆H₅CH₂OH in wastewaters

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Abstract

The heterogeneous oxidation of benzyl alcohol and formaldehyde in aqueous medium has been investigated. The catalytic oxidation of these compounds is carried out in the presence of Ni-oxide system at ambient temperature. The results show that under studied conditions, a 90% conversion of CH_2O to CO_2 and a complete oxidation of $C_6H_5CH_2OH$ to C_6H_5COOH is achieved. Addition of H_2SO_4 to adjust pH to 2 further precipitates benzoic acid. The precipitate is filtered and the resulting filtrate is free of organic substances (COD is below $10 \text{ mg } O_2 \text{ dm}^{-3}$). Based on the results obtained, a technology for purification of wastewaters containing benzyl alcohol as well as a catalytic method for degradation of CH_2O in aqueous solutions have been developed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Catalytic oxidation; Ni-oxide system; Detoxification of organic substances; Benzyl alcohol; Benzoic acid; Formaldehyde

1. Introduction

The degradation of organic pollutants, such as formaldehyde, benzaldehyde and benzyl alcohol, has attracted considerable attention due to the worldwide concern about the toxicity of these compounds. Wastewaters from different industries (pharmacy, perfumery and cosmetics, organic synthesis, manufacture of resin and colours, etc.) contain formaldehyde and benzyl alcohol in wide concentration ranges-from 0.5 to $10 \,\mathrm{g}\,\mathrm{dm}^{-3}$ [1]. The treatment of hazardous wastewaters, containing these pollutants in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. The biological processes which are preferably applied to treat wastewaters containing organic compounds do not always give satisfactory results, since many organic substances are resistant to biological treatment [2]. Low-temperature aqueous-phase catalytic oxidation is a promising alternative for the detoxification of wastewaters containing toxic substances. Catalytic oxidation reactions could

provide complete mineralization of organic substances while being environmental friendly.

Transient reaction at 273 and 300 K has been used to study the initial steps in the photocatalytic oxidation of benzyl alcohol and benzaldehyde absorbed on a thin film of TiO₂ catalyst by O₂ [3]. It was found that, in the course of oxidation reaction benzyl alcohol was first photocatalytically oxidized to benzaldehyde and then to CO_2 and H₂O.

Selective oxidation of benzyl alcohol to benzaldehyde was carried out over pumice-supported bimetallic and monometallic Pd and Ag catalysts. Preliminary kinetic studies were performed at 333 K in autoclave, at a pressure of 2 atm in pure oxygen. Under these conditions, small amounts of benzoic acid were detected [4].

Bessona and Gallezot [5] have studied the oxidation of aldehydes, alcohols or carbohydrate derivatives in aqueous medium with air in the presence of palladium and platinum catalysts under mild conditions (293–353 K and atmospheric pressure).

The present investigation aims at studying the possible development of an efficient catalytic method for the purification of wastewaters containing organic compounds using a low-temperature oxide catalyst.

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2. Experimental

2.1. Catalyst

A Ni-oxide system was used as a catalyst. It was synthesized, according to the procedure described in detail by Christoskova et al. [6]. The catalyst was characterized by means of IR, XPS, ESR, X-ray diffraction and chemical analyses. Analytical data obtained gave us reasons to conclude that under the applied conditions of synthesis of Ni-oxide with a high active oxygen content ($O^* \sim 8\%$), high degree of oxidation and octahedral coordination of the metal ions, and weak surface Ni-O bonds was obtained. The following formula of the oxide was suggested: Ni_x $(OH)_{\nu}O_{z}^{*}$ mH₂O, the metal cations on the catalyst surface being mainly in their highest oxidation state, i.e. +4. Due to these attractive properties, a high catalytic activity of the catalyst was expected in reactions of complete oxidation, carried out at low temperature.

2.2. Treatment conditions

The heterogeneous catalytic oxidation of benzyl alcohol and formaldehyde in aqueous solutions was carried out in a thermostated reactor under continuous stirring, thus providing an equal level of all parameters describing the state of the system (temperature, concentration, pH). The experimental runs were carried out as follows: the substrate solution was saturated with oxygen by bubbling air under atmospheric pressure for 30 min prior to adding the catalyst. Then the desired amount of catalyst (with particle size in the range 0.6-1.0 nm) was suspended in the solution. The application of the catalyst in the form of a suspension is more efficient because it leads to an increase in the catalyst surface accessible to the reaction. The air was continuously bubbled during the runs, thus maintaining a constant steady-state concentration of dissolved oxygen. After exhausting the active oxygen of the catalyst, the latter was regenerated with NaOCl.

The catalytic oxidation of formaldehyde was carried out using 1 M solution of CH₂O at pH 7.0, temperature 298 K and catalyst concentration of 0.5 or 2.0 g dm⁻³. The investigations concerning oxidation of benzyl alcohol were carried out with both model solutions containing 20 g dm⁻³ benzyl alcohol and wastewaters from "Hemus" plant, Bourgas, Bulgaria, containing from 15 to 20 g dm⁻³ benzyl alcohol. After complete conversion of benzyl alcohol into benzoic acid, the catalyst is filtered and 2 M H₂SO₄ was added to the filtrate and pH adjusted to 2.0. At this pH, white crystals of benzoic acid were precipitated. After separation of the crystals (by filtration) the liquid was neutralized with NaOH. The resulting solution is free of organic compounds and COD is below 10 mg O₂1⁻¹.

2.3. Analytical methods

The changes in the concentrations of benzyl alcohol and its oxidation products—intermediate benzaldehyde, and the final oxidation product benzoic acid, were monitored by UV–VIS spectroscopy and thin layer chromatography. The corresponding absorbance maxima of these compounds are at 205, 248, and 225 nm, respectively. Absorbance was measured with a Perkin Elmer Lambda-15 UV–VIS spectrophotometer.

Thin layer chromatographic analysis was carried out using standard chromatographic plates with silica gel 60 F_{264} support (E. Merck) and trichloromethane as eluent. The spots corresponding to benzyl alcohol, benzaldehyde and benzoic acid were developed with UV light.

The COD was determined according to standard procedure [7].

The initial and current concentrations of formaldehyde were checked by gas chromatography. GC analysis was performed with a Carlo Erba Fractovap 2400 T gas chromatograph equipped with an electrolytic conductivity detector. The operating parameters were as follows: temperature of the detector 473 K, temperature of the column (filled with 20% polyethyleneglycol on Chromosorb W)—383 K, carrier gas—hydrogen, volume of the analysed sample 2 µl. The retention times of CO₂, CH₂O, and HCOOH under the studied conditions were 30, 70, and 1624 s, respectively. The concentrations of CH₂O, CO₂ and HCOOH were calculated from the corresponding peak area, measured by means of an integrator.

The IR spectra of the fresh and used catalyst as well as the spectra of benzoic acid (product resulting in the heterogeneous oxidation of benzyl alcohol and commercially available reagent from E. Merck) were recorded with an FTIR-1750 Perkin Elmer spectrophotometer in KBr tablets.

The efficiency of the oxidation of benzyl alcohol and formaldehyde with the participation of Ni-oxide system under different conditions was evaluated through both the rate constant (k, \min^{-1}) and the overall degree of conversion $(\alpha, \%)$. The latter was calculated according to the equation

$$\alpha = \frac{C_0 - C}{C_0} 100,$$

where C_0 is the initial substrate concentration, mg dm⁻³, C is the current substrate concentration, mg dm⁻³.

The rate constant of the reaction of benzyl alcohol oxidation was estimated according to the first-order kinetic equation

$$k = \frac{1}{t} \ln \frac{A_{\infty} - A_0}{A_{\infty} - A_t},$$

where A_0 , A_t , A_∞ are the absorbances (determined from the recorded UV spectra) of benzoic acid at the beginning of the reaction (initial absorbance), at a fixed moment of the reaction and at complete conversion of benzyl alcohol into benzoic acid, respectively.

The activation energy $(E_a, kJ mol^{-1})$ was calculated from the rate constant vs. temperature plot according to the Arrhenius equation.

3. Results and discussion

3.1. Catalytic oxidation of formaldehyde

The change in formaldehyde concentration in the course of oxidation is illustrated by gas chromatograms represented in Fig. 1. The results of GC analysis show that a high degree of conversion of CH₂O to CO₂ and H₂O is achieved ($\alpha \sim 90\%$). The presence of HCOOH as an intermediate oxidation product was recorded (Fig. 1b). A catalytic oxidation of a model solution of HCOOH was carried out with a view to elucidating the oxidation mechanism. The concentration of HCOOH in the model solution was equivalent to the amount of

HCOOH produced in complete conversion of CH_2O into HCOOH under identical experimental conditions. It was established that a complete oxidation of HCOOH into CO_2 was achieved. These results gave us reasons to suggest that the catalytic oxidation of CH_2O proceeds according to a consecutive scheme:

$$CH_2O \xrightarrow{k_1} HCOOH \xrightarrow{k_2} CO_2$$
.

HCOOH was the only detected intermediate and its measured concentration in the course of the oxidation reaction was quite low. This is a reason to suggest that the rate of consumption of HCOOH is higher than the rate of its formation, i.e. the rate constant k_2 has a higher value than k_1 .

The results of kinetic investigations are illustrated in Figs. 2 and 3. Data presented are average results of three separate experiments and indicate that:

 a low-temperature catalytic oxidation of CH₂O with the participation of the synthesized catalyst proceeds under the studied conditions;



Fig. 1. Typical products detected by GC analysis during formaldehyde oxidation over Ni-oxide system: (a) 0 min; (b) 30 min; (c) 150 min.



Fig. 2. Kinetics of formaldehyde oxidation: $1 - \ln C = f(t)$; $2 - \alpha = f(t)$.



Fig. 3. The effect of the catalyst amount on the efficiency of the formaldehyde oxidation; catalyst concentration: $1-0.5 \text{ g dm}^{-3}$; $2-2.0 \text{ g dm}^{-3}$.

- a very high degree of degradation of formaldehyde to CO₂ has been achieved as proved by means of GC analysis. Fig. 1c shows that the conversion is approx. 90%;
- the catalytic oxidation of formaldehyde proceeds according to a pseudo-first-order kinetics with respect to substrate concentration, which is shown by the linear $\ln C$ vs. time plot (Fig. 2). Zero-order dependence with respect to oxygen was found under studied conditions due to the fact that all experiments were performed with continuous air bubbling through the liquid phase;
- the amount of catalyst influences the rate of formaldehyde degradation (Fig. 3). Evidently, the increase in the catalyst amount causes an increase in the oxidation efficiency. The rate constants of the oxidation process are 0.015 min^{-1} with m = 2.0 g and 0.007 min^{-1} with m = 0.5 g, respectively. This is a reason to suppose that the reaction proceeds only on the catalyst surface and is not homogeneous. An additional evidence for this conclusion is the fact that after removing the catalyst from the reaction mixture the oxidation process ceased. Moreover, no presence

of HO_2^- ion-radicals was detected in the liquid phase as it has been observed by Andreev et al. [8] by means of UV spectral analysis.

3.2. Catalytic oxidation of benzyl alcohol

The changes in the concentration of benzyl alcohol and its oxidation products during the process are illustrated by the UV spectra represented in Fig. 4. An isobestic point is evident which points out to the formation of a single intermediate (benzaldehyde), the latter being further oxidized to benzoic acid. Data obtained by thin-layer chromatography provide additional evidence that the transitions: $C_6H_5CH_2OH \rightarrow$ $C_6H_5CHO \rightarrow C_6H_5COOH$ take place.

The kinetic curves illustrating changes in the concentration of the starting compound and of the reaction products during the reaction are shown in Fig. 5. Calculations based on these data indicate that a heterogeneous catalytic oxidation of benzyl alcohol proceeds as a first-order reaction with respect to the alcohol concentration—the $\ln A_{C_6H_5CH_2OH}$ vs. time plot is a straight line (Fig. 6).

Data concerning the impact of reaction parameters such as temperature and mass of the catalyst, on the rate constant and on the time for complete degradation of benzyl alcohol are presented in Table 1 and Fig. 7. The results reveal that the studied factors influence significantly the efficiency of the catalytic process. It is seen that at 313 K and catalyst amount of 0.75 g, a complete degradation is achieved within 13 min. The value of the activation energy of the reaction was found to be 98 kJ mol^{-1} .

The results from the low-temperature catalytic oxidation of benzyl alcohol in an alkaline medium (pH 10–11) show that benzyl alcohol was selectively oxidized, its



Fig. 4. UV spectrum profiles during the oxidation of benzyl alcohol on the Ni-oxide system: a-e—absorbance maxima corresponding to C₆H₅COOH; a', b', c', d', e'—absorbance maxima corresponding to C₆H₅CHO.



Fig. 5. Concentration change of benzyl alcohol and reaction products during oxidation process.



Fig. 6. Linear transformation $\ln A_{C_6H_5CH_2OH} = f(t)$ of the kinetic curves of benzyl alcohol disappearance.

oxidation running practically completely to benzoic acid. In the course of the oxidation process, benzaldehyde is formed as an intermediate which is further oxidized to benzoic acid.

Fig. 8 shows the IR spectra of benzoic acid obtained after catalytic oxidation of wastewater from "Hemus" plant, Bulgaria (1) and of commercially available product from E. Merck (2). The comparison of the spectra shows that catalytic oxidation of benzyl alcohol on the Ni-oxide system results in benzoic acid of high purity. The analysis of the remaining solutions after removal of the benzoic acid shows that they do not



Fig. 7. The impact of the temperature on the kinetics of the benzoic acid formation; catalyst concentration 0.25 g.



Fig. 8. IR-spectra of the obtained benzoic acid (1) and the commercial product of E. Merck (2).

contain organic compounds (COD is below $10 \text{ mg} \text{ O}_2 \text{ dm}^{-3}$).

The low-temperature complete oxidation of CH_2O as well as oxidation of benzyl alcohol to benzoic acid with the participation of Ni-oxide system can be ascribed to the high content of weakly bonded surface-active oxygen on the catalyst which is responsible for the catalytic oxidation.

Table 1

The influence of the temperature and mass of the catalyst on the efficiency of the benzyl alcohol oxidation reaction

Temperature T (K)	Mass of the catalyst <i>m</i> (g)	Time for complete degradation t (min)	Rate constant $k \pmod{1}$	Activation energy $E_{\rm a} ({\rm kJ} {\rm mol}^{-1})$
293	0.25	230	0.010	98
293	0.75	63	0.048	
313	0.25	28	0.132	
313	0.75	13	0.450	



Fig. 9. IR spectra of the Ni-oxide system : (1) fresh catalyst; (2) after depletive oxidation of benzyl alcohol.

The present data are in agreement with both the results concerning activity and selectivity of the Ni-oxide system with respect to oxidation of other organic compounds as well as with the results of the characterization of the catalyst before and after oxidation reactions by means of different physical and chemical methods reported in a previous paper of ours [9]. Based on the summarized results some assumptions about the main steps in the oxidation of oxygen-containing organic compounds in the presence of Ni-oxide system can be made.

Most probably, the process is initiated by a dissociative adsorption of the substrate through α -H atom abstraction and formation of surface complexes. The latter, depending on the conditions, are decomposed to

the corresponding intermediates, or are further oxidized to carbonate complexes, which can subsequently produce CO_2 . The α -H atom released by the organic molecule forms OH radicals with the surface-active oxygen of the catalyst surface. These radicals possess very high reactivity and take part in the next stages of oxidation. In support of this statement, is the fact that during the depletive oxidation of the substrate the amount of active oxygen in the catalyst is continuously decreased as proved by chemical and IR spectral analysis. In the course of the oxidation process, the band at 586 cm⁻¹, characteristic of the valent vibrations of metal-oxygen bond on the surface of the Ni-oxide system, disappears from the spectrum and a new band at 3641 cm^{-1} appears (Fig. 9). The latter band is attributed to surface OH groups (formed between active oxygen of the catalyst and abstracted hydrogen atom). On regeneration of the reduced catalyst with NaOCl, the band at 3641 cm^{-1} disappears while that at 573 cm^{-1} reappears, i.e. these bands are generically related [6].

Based on these results and their interpretation, a probable mechanism of the catalytic oxidation of formaldehyde and benzyl alcohol with the participation of Ni-oxide system can be proposed, as shown in Fig. 10.

4. Conclusion

The results of the present study give us reasons to conclude that it is possible to realize the purification of wastewaters containing CH₂O and benzyl alcohol by



Fig. 10. Simplified reaction pathway of formaldehyde (a) and benzyl alcohol (b) oxidation reactions.

their catalytic oxidation over Ni-oxide system under mild conditions. A 90% conversion of formaldehyde to CO_2 can be achieved for 150 min at pH = 7.0, 298 K and concentration of the catalyst 2 g dm^{-3} . The complete degradation of benzyl alcohol to benzoic acid is achieved within 13 min at 313 K and catalyst amount of 0.75 g.

The results of the present investigation were used to develop a technological scheme, which was applied to purification of wastewaters from "Hemus" plant, Bourgas, Bulgaria [10]. The main advantage of the proposed catalytic method for purification of wastewater containing highly toxic organic compounds is that a very significant cleaning effect is achieved for a short time. This fact allows the treatment of wastewater of high flow at low temperatures ($25-36^{\circ}C$).

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