ROOM TEMPERATURE CATALYTIC DEGRADATION OF FORMALDEHYDE IN WATER OVER NANOSTRUCTURED Ni-OXIDE SYSTEM

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Abstract

Formaldehyde (HCHO) is regarded as one of the most versatile basic chemicals in various industries but it is hazardous for environment and living organisms. Therefore, it is imperative to remove it from wastewater which is directed to natural water. Heterogeneous catalytic oxidation of toxic substances in water with the participation of oxides of transition metals is an efficient approach for abatement these pollutants. In this study, nanostructured NiO_x was synthesized by ultrasound assisted precipitation-oxidation method and its catalytic properties for low-temperature complete oxidation of 50 mg/l HCHO with NaOCl in aqueous solutions were explored. The catalyst was characterized by XRD, FTIR spectroscopy, TEM, thermal and chemical analyses. The catalytic activity of NiO_x was evaluated through both the rate constant (k, min^{-1}) and the degree of HCHO conversion (α, %). The effect of several parameters on the HCHO degradation efficiency such as catalyst loading, temperature, and oxidant concentration was explored. By applying the method of the planned experiment the optimal conditions for achieving complete conversion of HCHO were determined (catalyst loading 1.5 g/l temperature 30^oC, and NaOCl concentration 15 ml/l).

Key words: *HCHO complete oxidation, NiO_x catalyst, NaOCl, wastewater treatment*

1. INTRODUCTION

Environmental protection is one of the major worldwide tasks of our times. As environmental regulations become more stringent, efforts are directed towards development of remedial solutions for industrial effluents treatment. Formaldehyde is a common chemical compound widely used in various industries such as synthetic resins and adhesives production, chemicals, pharmaceuticals and paper manufacturing, textile and wood processing, etc. (Moussavi et al. 2009, Pedersen et al. 2007). This compound has also non-industrial applications such as sterilization of sanitary parts and medical instruments. Due to its wide application, HCHO is frequently released in wastewaters, which when directed to natural water induces environmental pollution. Formaldehyde is toxic for living organisms and thus can cause serious health disorders (Silva et al. 2003, Zhao et al. 2012). Moreover, US EPA has classified formaldehyde as a "Probable Human Carcinogen" (Moustafa et al. 2002). Therefore, in order to prevent such ecological issues, it is essential to remove formaldehyde from wastewaters before discharging it into the environment. Thus, the treatment of such wastewaters in an environmentally acceptable manner and at a reasonable cost is a topic of great importance.

At present, the conventional methods used to treat wastewaters containing formaldehyde are biological, physical, and chemical processes. Biological treatment is one of the most common methods for purification of biodegradable compounds in water (Pereira and Zaiat 2009, Lotfy and Rashed 2002). However, the application of single biological process for the treatment of formaldehyde wastewaters is limited due to the inhibitory effect of HCHO on the metabolism of microorganisms and its high toxicity in high concentrations (800–1500 mg/l) so it always needs pretreatment by another method (Silva et al. 2003, Moussavi et al. 2009).

Adsorption method is an effective, easy to adapt to a specific system method that has many advantages: it is fast, cheap and universal (Boonamnuayvitaya et al. 2005). The most thoroughly used adsorbents for HCHO removal are activated charcoal, clay minerals, zeolites, various polymers, biosorbents, etc (Kulikauskaite and Paliulis 2015, Yousef et al. 2011, Salman 2012). However, the degradation of HCHO could not be achieved using non-destructive adsorption process, i.e. the contaminants still exist in the whole environment. Moreover, new secondary waste could be generated

that required further treatment and thus increasing the operation cost.

Chemical oxidation is traditionally accepted as the most promising alternative for the degradation of persistent pollutants with limited biodegradability and tendency to accumulate in the environment. This method is one of the simplest destructive technologies based on conversion of the pollutants contained in wastewaters to harmless products under the effect of strong oxidizers, such as ozone, H_2O_2, sodium hypochlorite (NaOCl) (Melero et al. 2009). Non-catalytic wet air oxidation (WAO) usually requires high temperatures (180–315°C) and pressures (20–150 bar) (Luck 1999). In fact, only 38% degree of HCHO conversion for 180 min at temperature of 200°C and pressure up to 35 bar has been achieved (Pintar et al. 2004, Zou et al. 2007 - Eco 2016 paper). Milder operating conditions, increasing also the oxidation rate and consequently lower costs in pollutants removal has been achieved in the catalytic wet air oxidation (CWAO) (Silva et al. 2003, Raumchat et al. 2006, Levec and Pintar 2007, Gutiérrez-Arzaluz et al. 2016). Although in much case homogeneous catalysts are more effective than heterogeneous ones, generation of secondary pollutants such as metal ions in solution requires additional treatment step for their removal from the wastewater.

As a viable and promising alternatives to the chemical oxidation strategy for destroying toxic compounds are considered advanced oxidation processes (AOPs), involving Fenton, Fenton-like or the photo-Fenton processes, photolysis, photo- or catalytic ozonation, photocatalysis. These processes are based on of strongly reactive radicals ($^{\bullet}OH$, $O_2^{\bullet-}$, $SO_4^{\bullet-}$) which can easily attack and destroy organic molecules to harmless products (CO_2 and H_2O). AOPs have demonstrated attractive merits including complete decomposition, room temperature operation, and generation of less harmful and more biodegradable final products (Sun and Wang 2015). Nonetheless, the main disadvantages of AOPs are the requirement of a very low pH, specific equipment, high energy inputs and the usage of a dangerous and unstable oxidant.

Heterogeneous catalytic oxidation is an alternative and promising solution for all the foregoing issues, since catalytic reactions can be carried out under mild operating conditions (room temperature and atmospheric pressure) and using simplified apparatuses. Hence, development and design of active catalysts for oxidative degradation of formaldehyde present in wastewaters is of great importance. Effective catalysts for degradation of formaldehyde in an aqueous solution are developed on the basis of noble metals (Zhang et al. 2009, Peng et al. 2007). Using Pd/TiO_2 catalyst a complete room temperature air oxidation of HCHO has been achieved (Huang and Leung 2011). It has been suggested that Pd- nanoparticles acts as active centers for activation of oxygen. Platinum nanoparticles incorporated in calcium phosphate particles are found as effective catalysts for the oxidative degradation of formaldehyde in water with dissolved oxygen from air as an oxidant (Fam and Imae 2015). The reaction is operated at atmospheric air pressure and mild temperatures and almost 100% HCHO decomposition can be achieved for 4 hours. Although excellent catalytic properties of noble metals, their high price has got a negative effect on the economic expedience of the process. As alternative, catalysts based on transition metals and their oxides (Ni, Fe, Cr, Mn, Co), deposited on appropriate supports (Al_2O_3, CeO_2) have been proposed. It has been reported that for the complete oxidation of HCHO on MnO_x – CeO_2 important role has played the higher oxidation state of the Mn – ion and the larger amount of mobile oxygen at the surface (Tang et al. 2006). In our previous paper (Stoyanova et al. 2016) we have studied the catalytic degradation of formaldehyde in water phase over nonstoichiometric CoO_x. It was found that the as-prepared catalysts exhibited high catalytic activity selectivity in the complete oxidation of formaldehyde at ambient conditions.

The aim of the present study was to investigate the catalytic performance of the NiO_x in reaction of complete oxidation of HCHO with NaOCl in aqueous solution at a low temperature and under atmospheric pressure. The kinetics of the oxidation process and the effect of various operating parameters influencing HCHO degradation efficiency such as the catalyst amount, NaOCl concentration, and reaction temperature were studied. Moreover, the optimal technological parameters of the process were determined by applying the method of the planned experiment.

2. EXPERIMENTAL PART

2.1. Catalyst preparation and characterization

The NiO_x catalyst was synthesized by ultrasound assisted precipitation-oxidation method with reverse order of precipitation. A certain volume of nickel nitrate aqueous solution (1 M) was added to a mixture of aqueous solutions of NaOH (4M) and NaOCl (1 M) under continuous stirring. The resulting black precipitate was pretreated for 20 min with the ultrasonic homogenizer UP100H and allowed to stay in mother liquor for 24 hours. Then the solid was filtered, washed with distilled water until negative reaction for Cl- and neutral pH, followed by drying at 105°C overnight.

2.2. Characterization of catalysts

The synthesized NiOx system was characterized by means of X-ray diffraction (XRD), chemical and thermal analyses, transmission electron microscopy (TEM), and FTIR spectroscopy.

The chemical analysis of the catalyst included determination of the active oxygen content (total and surface), the content of nickel in gram sample, as well as determination of the NiO_x solubility at different pH values of the medium.

Active oxygen is the amount of over-stoichiometrical oxygen in the oxide above that corresponding to the lowest stable oxidation state. The total active oxygen content (O*) was determined by a direct iodine method (Nakagava et al., 1962). A sample (0.1g) was dissolved in dilute (1:10) sulphuric acid containing 2g of potassium iodide. The solution was magnetically stirred and after a complete decomposition the liberated iodine was titrated with standardised 0.1 N sodium thiosulphate using starch as indicator. The relative standard deviation of the method is 4.71%.

The total active oxygen content in g-at.g^{-1} and % was determined according to the equations:

$$O^* = \frac{N \times V \times mgE_{O_2}}{m \times 16}, g-at/g \qquad O^* = \frac{N \times V \times mgE_{O_2}}{m} \times 100,\%$$

where: N – normality of the titrant; V – volume of the consumed titrant solution, cm^3; m- catalyst amount, g; $mgE_{O_2} = 0.008$, miligram equivalent O_2.

The amount of surface active oxygen (Os*) was determined by the hydrazine method (Ushijima et al., 1967). A known amount of 0.1 N hydrazine sulphate solution is allowed to react with a known weight of catalyst sample for about 20 min in a closed vessel. The residual hydrazine after filtration was titrated against 0.1 iodine solution at pH = 7.2. The relative standard deviation of the method is 5.02%.

The amount of nickel in the prepared sample was measured by atomic absorption spectroscopy (AAS, Perkin-Elmer) at the corresponding resonance wavelength.

XRD was performed using a X-ray diffractometer TUR-MA 62, operating at U = 37kV, Cu Kα radiation (λ = 1.5406 Å) and I = 20mA. The diffractometer was supplied with a computer-contolled goniometer (HZG -3), scanning step of the spectrum of 0.04^0 and collection time of impulses - 1.2 s. The samples were scanned in 2θ range within 10 - 80^0. The FTIR spectra were taken on a 1750 Perkin Elmer spectrophotometer, with 2 cm^{-1} resolution, in KBr tabletes (1 mg of the corresponding sample in 100 mg KBr). The differential thermogravimetry (DTG), differential thermal analysis (DTA) and thermogravimetry (TG) curves were taken with a Derivatograph Q in air under the following conditions: mass of the sample 0.1 g, sensitivity 0.5 mV for DTA, 1.8 mV for DTG and 0.1 mV for TG; temperature range 20 - 1000°C; heating rate 10°C min^{-1}.). The surface morphology of the NiOx was characterized on high-resolution transmission electron microscope JEOL JEM 2100 operating at an accelerating voltage of 200 kV.

2.3. Experimental procedure

The catalytic oxidation of HCHO was carried out in a 400 mL thermostated reactor at batch mode with constant stirring throughout the reaction at around 400 rpm to ensure continuous contact between the

solution and catalyst. In a typical run, 200 ml 50 mg/L HCHO aqueous solution was saturated with oxygen by bubbling air under atmospheric pressure for 30 minutes. Then a predefined volume of 10% aqueous solution of NaOCl was added into the solution. The experiment was initiated by the addition of a fixed amount of catalyst. At specific time intervals, samples of 5 ml were withdrawn from the suspension and were centrifuged at 4000 rpm for 1 min to remove the catalyst. The concentration of HCHO in the filtrate was monitored spectrophotometrically (λ_{max}=565 nm) using Spectroquant® Formaldehyde test (Merck), compatible with the spectrophotometer NOVA 400 (Merck). The UV–Vis spectra as well as their first derivatives (D1) were recorded by two-beam scanning UV-Vis spectrophotometer (Cintra 101) in the range of 400-700 nm. Depletive oxidation experiments (without adding of NaOCl) were also performed in order to clarify the reaction mechanism.

The efficiency of the oxidation process was assessed by the degree of HCHO conversion at a given moment during the course of the reaction (α, %), calculated using following equation:

$$\alpha = \frac{C^o - C}{C^o} 100, \%$$

,

and by the rate constant (k, min^{-1}), determined by the kinetic equation of a first-order reaction:

$$k = \frac{1}{t} \ln \frac{C^o}{C}$$

where C^o and C are the initial and the HCHO concentration at time t (mol/l), respectively.

All experiments were conducted in triplicate to ensure the reproducibility of experimental results.

3. RESULTS AND DISCUSSION

3.1. *Characterization of the NiO_x catalytic system*

Chemical analysis

Data about both nickel and active oxygen content in as-prepared catalyst, as well as the solubility of the NiO_x at different pHs'are presented in Table 1 and Fig.1.

Table1. The content of active oxygen and nickel in the NiOx

Catalyst	***Active oxygen content***				***Nickel content***
	total (O*)		surface (O_s*)		
	g-at.g^{-1} .10^3	%	g-at.g^{-1} .10^3	%	g-at.g^{-1} .10^3
NiO_x	3.33	5.33	2.41	3.89	5.61

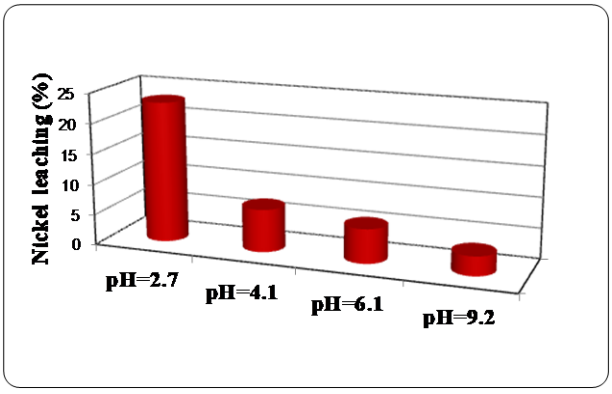

Fig.1. Influence of pH on the solubility of NiO_x

Analysis of the results listed in Table 1 reveals that the applied synthesis method favors the formation of nonstoichiometric oxide system characterized by high content of active oxygen. Moreover, the surface active oxygen constitutes about 73 % of O*. It should be noted that the Ni-oxide system completely loses its active oxygen at temperatures higher than 433 K.

As seen from Fig.1, the catalyst demonstrated a very low solubility at pHs higher than 4 (under 5%), indicating for high stability of NiO_x under the effect of the reactive medium and, respectively, for the ability to preserve the initial activity at multiple use in the catalytic reaction.

Powder X-ray diffraction (XRD)

The results of XRD analysis have revealed that an amorphous Ni-oxide system was obtained by the applied synthesis procedure. The amorphous character of the sample suggests that the active sites are isostructural and chemically identical, which is a prerequisite to high activity in oxidation reactions.

Infrared spectral analysis (FT-IR)

The FT-IR spectra of NiO_x – fresh and calcined at different temperatures are presented in Fig.2. Distinct absorption band is visible at 573 cm^{-1} in the spectrum of the fresh sample, which is provided by stretching vibrations of the metal–oxygen bond on the oxide surface. This band accounts for the presence of active oxygen in the sample as its intensity is proportional to the O* content in the catalyst. The active oxygen content decreased almost two-fold by heating the NiO_x at 120°C and was completely reduced at thermal treatment at temperatures higher that 160°C.

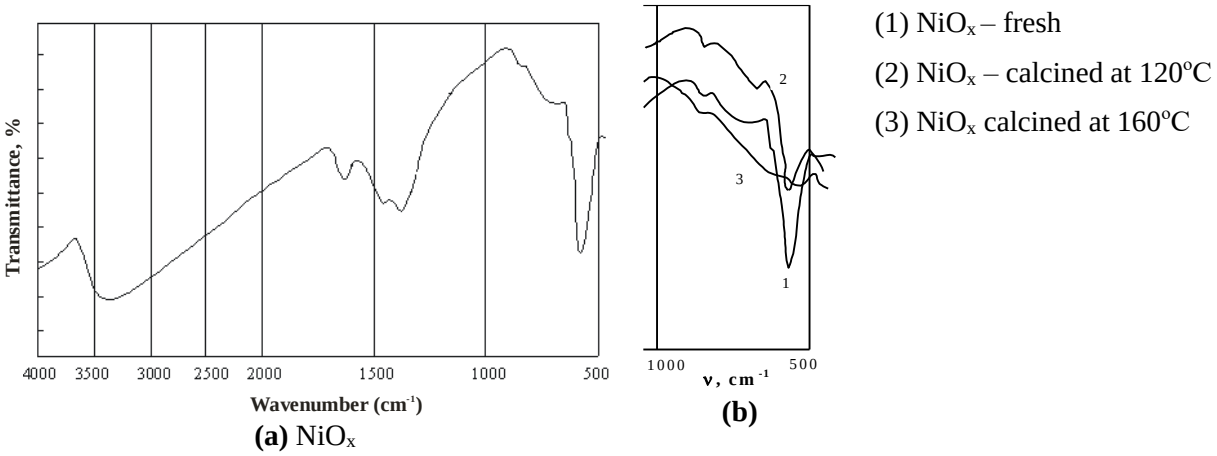

Fig.2. FT-IR spectra of (a) NiO_x – fresh and (b) thermally treated at different temperatures

X-ray photoelectron spectroscopy (XPS)

The oxidation state of Ni in the synthesized catalytic system was determined by means of X-ray photoelectron spectroscopy. O1s and $Ni2p_{3/2}$ lines of NiO_x in the X-ray photoelectron spectra are presented in Fig.3.

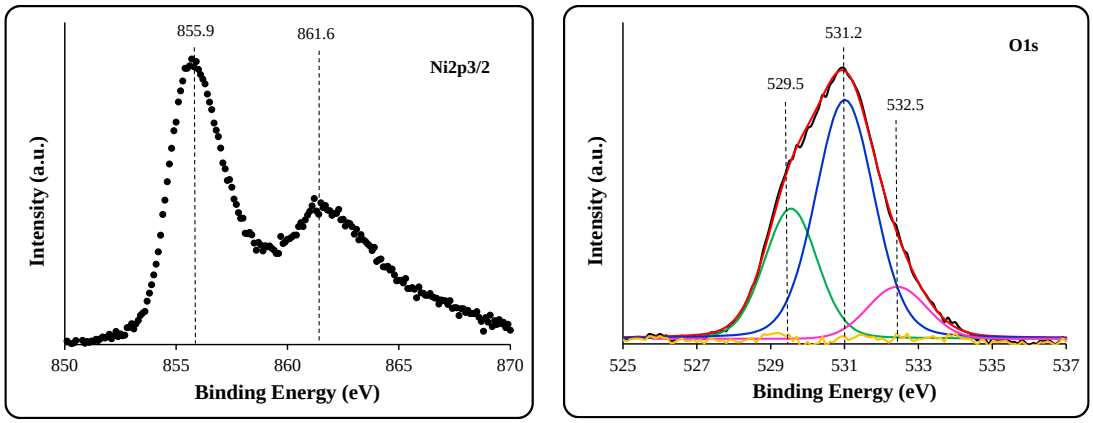

Fig.3. Ni2p$_{3/2}$ and O1s envelopes of NiO$_x$

The Ni 2p3/2 profile displayed a main peak centered at 855.9 eV with its shake-up satellite around 6 eV to higher binding energy. As the binding energy (BE) of Ni ions in the synthesized catalyst is higher than the typical for Ni^{2+} in stoichiometric NiO (854.6 eV), it could be suggested that the the NiO_x catalyst is shown to expose surface $Ni^{\geq+3}$. Asymmetrical profile of the O1s line in the XPS spectrum of NiOx indicates for the simultaneous presence of various oxygen particles. Three peaks subpeaks with BE of 529.5, 531.2 eV, and 532.5 eV appear after deconvolution of the O1s envelop, which were identified to be lattice oxygen species, surface OH groups or O^- species adsorbed on the catalyst surface, and intercalated water molecules, respectively. Quantitative data of the XPS analysis show that the main part of oxygen in the sample is bonded as hydroxyl groups or exists as O^- ions.

Thermal analysis

Although the freshly obtained NiO_x is an X-ray amorphous one, the thermal analysis revealed clearly that the catalyst underwent transformation with increasing the temperature from ambient degree to 1000∘C in several steps (Fig.4).

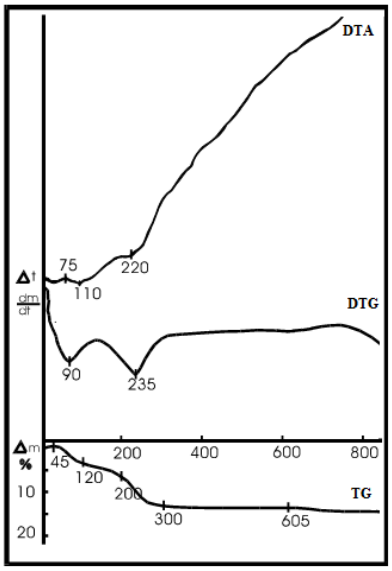

Fig.4. DTA, DTG and DTG profiles of the as-prepared NiO$_x$

Two endo-effects have been registered in the DTA and DTG curves of NiO_x. The first endo-effect at around 90°C could be attributed to the release of active oxygen leading to a color change of the sample

(from black to gray). The reduction of the O* content (confirmed by chemical analysis) continues until 160°C and brings a weight loss of around 13%. The endo-effect at 235°C could be ascribed to the release of either crystal water or OH groups and simultaneously formation of NiO. The subsequent exo-effect as probably associated with the crystallization of the NiO.

TEM analysis

Fig. 5 shows the TEM image of the cobalt–ferrite nanocrystals deposited on a carbon coated copper grid. As seen from Fig. 1a the NiO_x nanoparticles have spherical form and diameter in the range 5 nm - 20 nm. The crystalites form large agglomerates containing hundreds of particles.

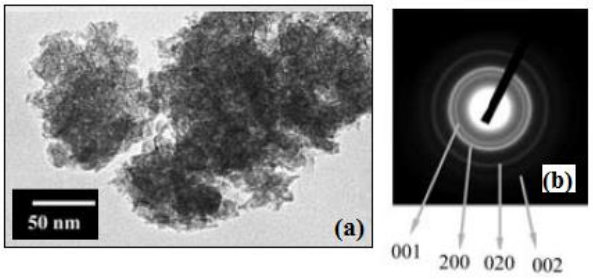

Fig. 5. TEM micrographs of the synthesized NiO_x:(a) bright field TEM, (b) SAED pattern

The well-defined rings observed in the SAED pattern obtained from TEM (Fig. 6b) confirm the nanocrystalline nature of the material. The diffraction rings indexmatched to those of non-stochiometric monoclinic $Ni_{15}O_{16}$ [PDF 72-1464].

3.2. Catalytic activity of NiO_x in a reaction of complete HCHO oxidation with NaOCl in water

3.2.1. Chemical oxidation of HCHO

Initially, in order to confirm the expediency of introducing catalyst into the HCHO – oxidant system, control experiments of chemical oxidation of formaldehyde were carried out using 30% solution of H_2O_2 and 10% solution of NaOCl alone as oxidants. Results showed that under studied conditions only 70% of HCHO was oxidized for 20 min with stoichiometric and twofold amounts of H_2O_2, however, the formed formic acid has not undergone further oxidation even at complementary adding of H_2O_2. When NaOCl (5 ml/l) was used as oxidant, the chemical oxidation of formaldehyde (50 mg/l) proceeds with a low rate and only 39% removal efficiency could be reached for 90 min. Obviously, sodium hypochlorite itself has limited ability to oxidize HCHO although it is a strong oxidizing agent. Consequently, chemical oxidation of HCHO with NaOCl will be ineffective for treating large volumes of wastewaters and thus this method is not very promising at an industrial level. These unsatisfactory results directed us to examine the possibility for increasing the effectiveness of the oxidation process through intoducing a catalyst into the system.

3.2.2. Catalytic oxidation of HCHO with NaOCl over NiO_x

The results of the comparative study of the kinetics of oxidation of HCHO in various systems are displayed in Fig.6.

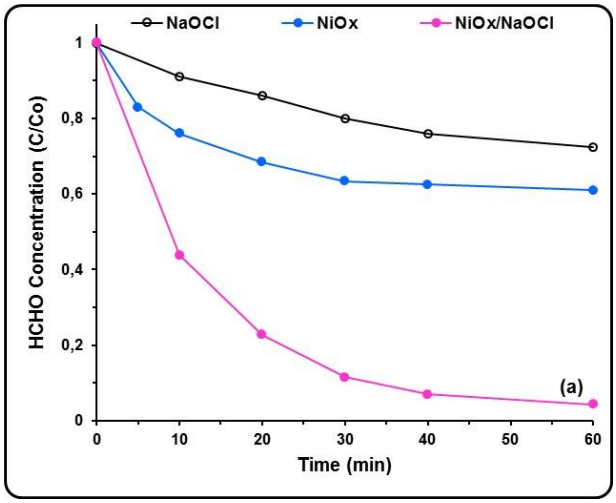

Fig.6. Comparative kinetics of chemical, depletive and catalytic oxidation of HCHO (50mg/l HCHO, 5 ml/l NaOCl, 1.0 g/l catalyst, 20°C)

It is seen from the presented data that whitout use of a catalyst the oxidation of formaldehyde has proceeded with low rate – only 28% degree of HCHO oxidation was achieved in one hour. In the presence of NiO_x but without addition of oxidant (depletive oxidation), nearly 36% of HCHO was degraded for 30 min but its concentration was kept unchanged afterwards. The HCHO degradation profile under these conditions could be explained by assuming that HCHO is oxidized by the active oxygen of the catalyst and, at its depletion, the oxidation process has been stopped. This assumption was confirmed by chemical analysis (around 10-fold decrease in the O* content) as well as by comparison of the FTIR spectra of the catalyst, recorded before and after depletive oxidation of HCHO (Fig. 7). An obvious decrease of the band intensity at 573 cm^{-1} in the FTIR spectrum of NiO_x pointed out for the reduction of the amount of active oxygen in the catalyst.

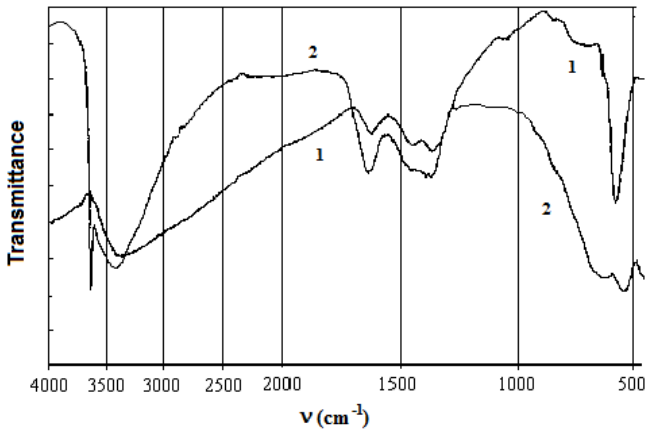

Fig.7. FTIR spectra of NiO_x before (1) and after depletive oxidation of HCHO (2)

A simultaneous presence of heterogeneous catalyst and oxidant led to significant enhancement of the HCHO oxidation rate as compared to the chemical and depletive oxidation ones. Degradation of HCHO as high as 97% could be achieved for 60 min under similar conditions as evidenced by the changes observed in the UV-Vis spectrum of HCHO in the course of catalytic oxidation on NiO_x as

well as its first derivatives (Fig. 8). Three-fold increase in the concentration of catalyst (3 g/l) and oxidant (15 ml/l) leads to a sharp increase in the reaction rate and a complete oxidation of formaldehyde within a short duration of 5 min was already reached (Fig. 9b). In contrast to the depletive experiments the active oxygen content in the spent catalyst was almost equal to that in fresh NiO_x. Thus, it may be speculated that NaOCl has provided a permanent regeneration of the O* that has been consumed in the course of formaldehyde oxidation.

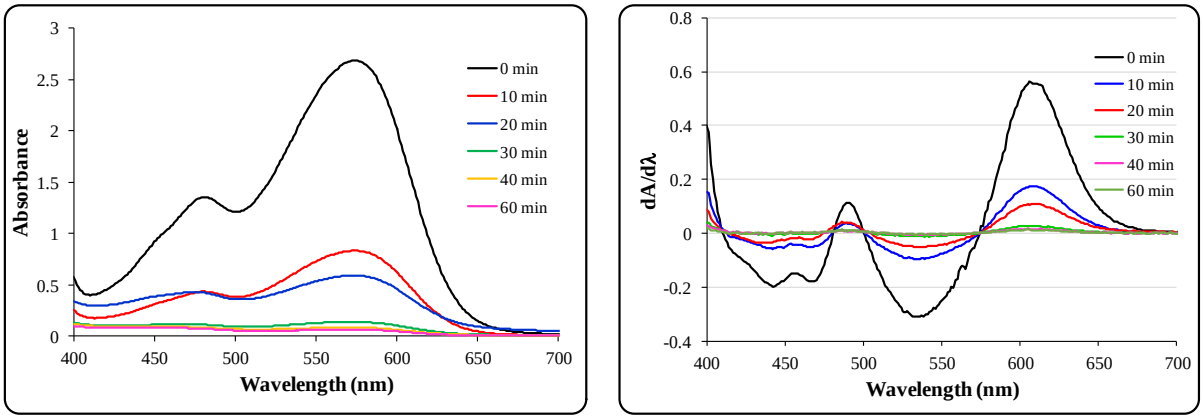

Fig.8. UV-Vis spectra and their D1 derivatives recorded during the HCHO oxidation on NiO_x (50mg/l HCHO, 5 ml/l NaOCl, 1.0 g/l catalyst, 20°C)

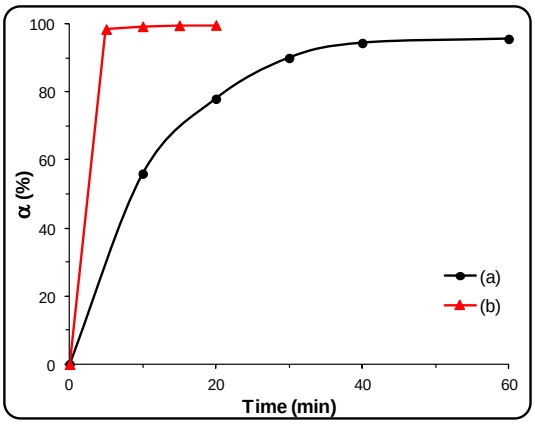

Fig.9. Degree of HCHO conversion with time: (1) 1.0 g/l NiO_x, 5 ml/l NaOCl; (2) 3.0 g/l NiO_x, 15 ml/l NaOCl

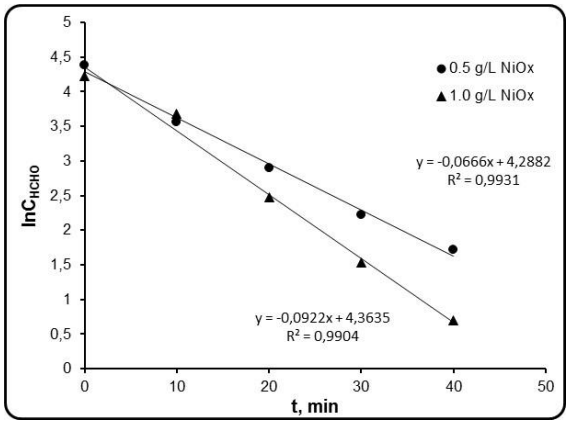

Fig.10. Linear transformation of the kinetic curves of HCHO catalytic oxidation over NiOx (5 ml/l NaOCl, 20°C)

The assumed first-order kinetics of HCHO decay was confirmed by the linear plots of ln (C_o/C) versus time (Fig. 10).

The method of the planned experiment has been applied for determination of the optimal technological parameters of the process. Complete factor experiment of the type $N = 2^n$ has been implemented for determination of the values of both objective functions to maximise (response factors): Y_1 – degree of HCHO degradation in the 20th minute from beginning of the process, $\alpha_{20'}$, % and Y_2 – the rate constant k, min^{-1}. As independent variables (factors) were chosen: X_1 – concentration of the catalyst (g/l); X_2 – concentration of the oxidant (ml/l); X_3 – temperature (°C). The basic levels of the factors and the intervals of their variations, determined on the base of analysis of the results of preliminary experiments, are presented in Table 2.

Table 2. Basic levels and intervals of variation of the independent variables

Variables	[X_i]	Interval of variation, λ_i	Levels of the variables		
			$X_i = -1$	$X_i = 0$	$X_i = +1$
X_1	g/l	0.5	0.5	1.0	1.5
X_2	ml/l	5.0	5.0	10.0	15.0
X_3	^oC	5.0	20	25	30

The practical realization of the experiment has been realized on the base of the composed plan-matrices following the principle of randomization of the trials. It has been worked with double trials in order to make it possible to check for the homogeneity of the dispersions throughout the entire factor space. The results obtained in studying the influence of the three factors on the degree of HCHO degradation in 20 min and on the rate constant are presented in Table 3.

Table 3. Plan-matrices and experimental results of the experimental design for HCHO oxidation over NiO_x catalytic system

Run No.	X_1 g/l	X_2 ml/l	X_3 ^oC	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y_1 ($\alpha_{20'aver.}$)	Y_2 ($k_{aver.}$)
1	0.5	5.0	20	+	+	+	–	86.25	0.088
2	1.5	5.0	20	–	–	+	+	98.20	0.221
3	0.5	15.0	20	–	+	–	+	96.51	0.153
4	1.5	15.0	20	+	–	–	–	96.90	0.350
5	0.5	5.0	30	+	–	–	+	96.73	0.205
6	1.5	5.0	30	–	+	–	–	97.85	0.428
7	0.5	15.0	30	–	–	+	–	96.85	0.281
8	1.5	15.0	30	+	+	+	+	97.00*	0.757

** Degree of HCHO conversion in 5th minute.*

The coefficients of the following regression equations have been calculated on the basis of the obtained results:

$$Y_1 = 95.8 + 1.7X_1 + 1.03X_2 + 1.32X_3 - 1.56X_1X_2 - 1.38X_1X_3 - 1.21X_2X_3 + 1.32X_1X_2X_3$$

$$Y_2 = 0.31 + 0.13X_1 + 0.07X_2 + 0.11X_3 + 0.04X_1X_2 + 0.05X_1X_3 + 0.03X_2X_3 + 0.02\ X_1X_2X_3$$

The analysis of the obtained regression equations show positive effect of the studied factors on the effectiveness of the catalytic process. Maximum purification effect for shortest time (*ca.* 5 min) was achieved at upper level of the three factors (Run No. 8), while the lowest rate of the oxidation process was observed at run No.1 (lower level) – complete oxidation of formaldehyde has been attained in *ca.* 35 min. It should be emphasized that complete oxidation of HCHO to CO_2 and H_2O has been practically attained with all combinations of the variables proved with gas-chromatographic analysis (Fig. 11).

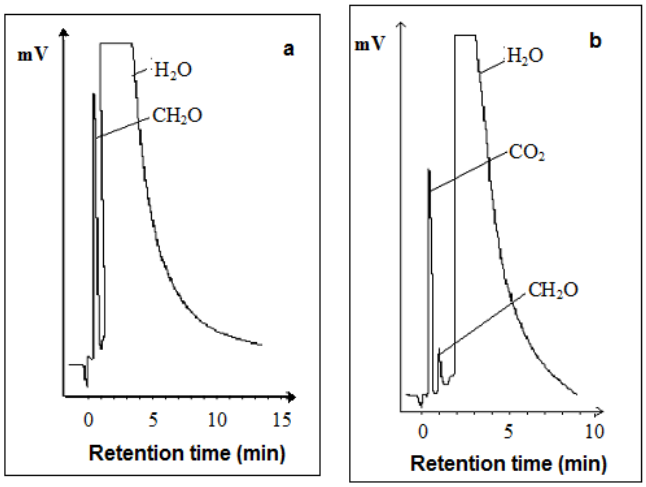

Fig.11. GC analysis of reaction mixture during catalytic oxidation of HCHO over NiO_x: (a) 0 min; (b) 5 min (50 mg/l HCHO, 1.5 g/l NiOx, 15 ml/L NaOCl, 30◦C)

The amount of the catalyst (factor X_1) exhibited the strongest influence on rate of the catalytic process (Fig.12). In fact, the rate constant has increased *ca*. 2.5 times at three-fold increase of the catalyst amount with identical other factors – temperature and concentration of the catalyst (Fig.13).

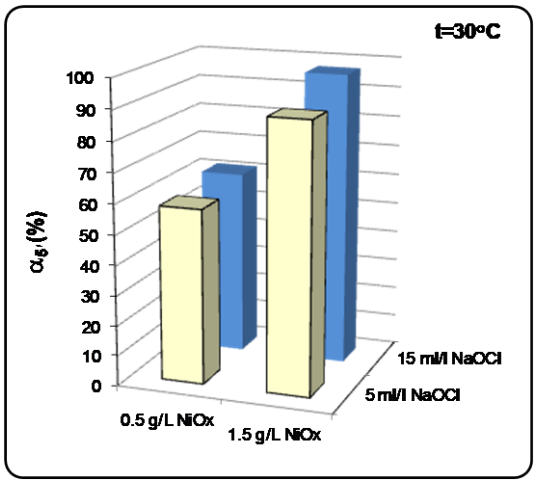

Fig.12. Combined effect of the studied variable factors on the degree of HCHO catalytic oxidation over NiO_x at 5th minute

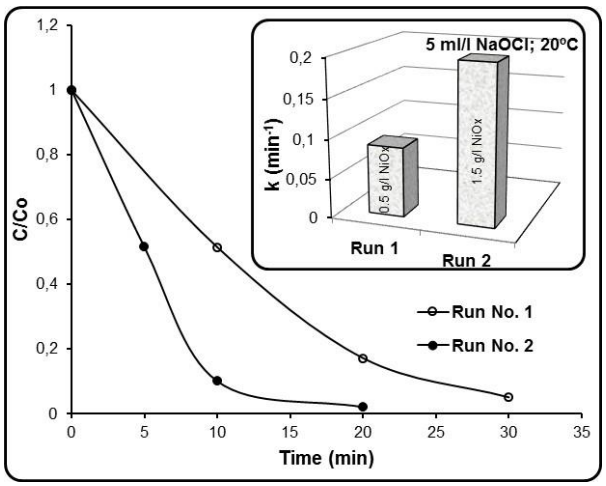

Fig.13. Effect of catalyst amount on the HCHO degradation rate

Results obtained also show that the time for complete oxidation of formaldehyde is reduced almost twice by increasing the reaction temperature with 10°C (Fig. 14a), while the effect of oxidant concentration on the reaction kinetics is less pronounced – less than two-fold increase in the rate constant is observed with increasing NaOCl concentration from 5 ml/l to 15 ml/l (Fig. 14b).

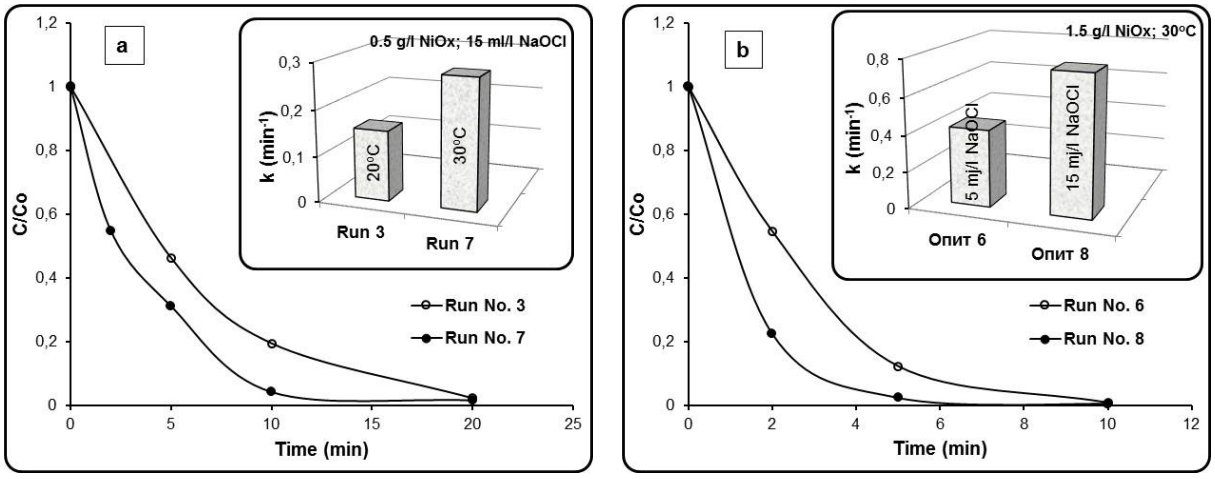

Fig.14. Influence of reaction temperature (a) and concentration of NaOCl (b) on the HCHO catalytic oxidation with participation of NiO_x

4. CONCLUSIONS

From the presented data, it can be concluded that the present investigation proposes an advantageous catalytic method, where the oxidation reaction is operated at atmospheric pressure and room temperatures and complete oxidation of formaldehide can be achieved. The synthesized catalytic system exhibited very high activity in the studied reaction. Using 1.5 g/l NiOx, conversion rate of more than 98 % has been achieved for 5 minutes at 30°C. Nanosized NiO_x catalyst also demonstrated stable performance during the recycling test and therefore will be good candidate as catalytic material for environmental applications including the treatment of effluents containing formaldehyde. Process optimization showed that the studied operational parameters were the effective and adjustable factors that could be used to accelerate the oxidative degradation of HCHO in an aqueous solution. However the conditions that must be chosen for the practical application of the proposed catalytic method depends on the output of wastewaters, the concentration of HCHO in the wastewaters, and the capacity of the purification installations.

ACKNOWLEDGEMENT

Authors gratefully acknowledge financial support by the National Science Fund (Project DFNI-T02/4) and by the University of Plovdiv Research Fund (Project NI 17 HF).

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