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Catalytic oxidation of formaldehyde in aqueous solutions over NiO_x/CeO_2

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The catalytic performance of NiO_x supported on CeO_2 prepared by modified precipitation-oxidation method for the complete oxidation of formaldehyde (HCHO) with NaOCl in aqueous solutions was explored. The as-prepared catalyst was characterized by XRD, HRTEM, FTIR and chemical analyses. It has been found that under the applied synthesis conditions nanosized and well dispersed on the surface of CeO_2 non-stoichiometric $Ni_{15}O_{16}$ oxide was obtained. The catalytic activity of the NiO_x/CeO_2 was found better than both the unsupported bulk analogue and physical mixture of NiOx and CeO_2, suggesting a synergistic effect of active oxide phase and support. The effect of main operational parameters influencing HCHO degradation efficiency such as catalyst loading, temperature, and oxidant concentration were studied. Factorial experimental design approach was applied to assess the effects of these parameters on the effectiveness of the oxidation process. Results obtained revealed that the optimal conditions for achieving fast and complete degradation of HCHO are temperature 30°C, catalyst loading 1.5 g dm^{-3}, and NaOCl concentration 15 ml dm^{-3}. Therefore, NiOx/CeO_2 catalyst can be successfully used for the treatment of wastewaters with high concentration of formaldehyde.

***Key words**: formaldehyde, catalytic oxidation, NiO_x/CeO_2 catalyst, NaOCl.*

INTRODUCTION

Formaldehyde (HCHO) is a key compound in organic synthesis, widely used in many industrial activities such as synthesis of resins, medicinal products, drugs and others, too numerous to be mentioned. Therefore, wastewaters arising from these industrial manufactures may contain significant amounts of formaldehyde, which is considered as highly toxic and carcinogenic compound even at low concentrations. Thus, frequently release of HCHO in water systems may cause serious environmental pollution and risk for the surrounding biological populations.

Effluents containing high concentration of formaldehyde, 2000 – 4000 ppm, are traditionally treated by biological methods because of their low cost and simplicity [1, 2]. However, it has been found that these concentrations are toxic for the bacterial cultures used, and thus the biological treatment could be easily inhibited by damaging the DNA of the microorganisms [3]. Wet oxidation processes (WO) have been used in the treatment of HCHO containing wastewaters. In this method, the oxidation reaction takes place in aqueous phase where the formaldehyde molecules are oxidized with pure oxygen or air at high temperatures (180 – 315°C) and pressures (up to 150 bar). However, in this case many intermediate products have been detected, such as carboxylic acids, which is therefore necessary of a post-treatment stage [4]. Catalytic wet oxidation (CWO) is an interesting and advanced alternative to WO, since the harmful molecule can be completely oxidized into CO_2 and water in the presence of solid catalyst at milder reaction conditions.

Silva *et al.* have used several heterogeneous composite metal catalysts for oxidation of high formaldehyde containing industrial effluents (800 – 1500 ppm). The reaction has been carried out in a high-pressure reactor at 190 – 220 °C and 15 - 35 bar of pressure. It has been found that the Mn/Ce catalyst is the most active among the Mn/Ce, Co/Ce and Ag/Ce catalysts, leading to 99.4 % TOC conversion. Moreover, the application of the Mn/Ce catalyst for treatment of wastewaters from formaldehyde industry has been also discussed [5].

Pt/Al_2O_3 catalyst has been tested in CWO reaction for formaldehyde oxidation at 80 °C. It is shown that 80 % elimination of HCHO with initial concentration of 200 ppm, has been achieved for 4 hours. However, byproducts such as acetic and oxalic acids have been also determined [6].

A combination of catalytic advanced oxidation process of $O_3/MgO/H_2O_2$ with biological treatment has been used for complete mineralization of concentrated formaldehyde wastewaters. It has been shown that 98 % of COD removal has been achieved after 24 hours of reaction under optimum conditions

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– 5 g/L MgO powder, pH = 8, and 0.09 mol/L H_2O_2. Radical oxidation mechanism has been also proven [7].

It should be noted that the literature data concerning the catalytic oxidation of formaldehyde in liquid phase is very scarce. Therefore, it is important to develop an efficient, cheap and stable catalyst for complete oxidation of HCHO in aqueous phase. The aim of the present study is to synthesize and characterize the supported NiO_x/CeO_2 catalyst and to explore its catalytic activity for low-temperature complete oxidation of HCHO in aqueous solutions using NaOCl as oxidant.

EXPERIMENTAL

The NiOx/CeO_2 catalyst was prepared by deposition-precipitation technique with reverse order of precipitation. Solid CeO_2 (Aldrich) was suspended in a fixed volume of 0.1 M aqueous solution of $Ni(NO_3)_2.6H_2O$, in an amount necessary to achieve an atomic ratio of Ni:Ce = 1:1, followed by dropwise addition of a mixture of 4 M NaOH and NaOCl at constant stirring by the ultrasonic homogenizer to yield a black precipitate. The latter was allowed to age in the mother solution for 24 hours, followed by filtration, washing with distilled water to a negative reaction towards Cl^- ions and neutral pH. The precipitate was dried at 105 °C to constant mass. For comparison, bulk NiOx was prepared according to the same procedure but in the absence of CeO_2.

X-ray diffraction measurement (XRD) was performed using TUR-MA 62 (Germany) diffractometer with filtered Cu Kα radiation (λ = 1.5406 A) at U = 37 kV, and I = 20 mA, equipped with a computerized HZG-4 goniometer. The phase identification was carried out using JCPDS database. The FTIR spectra were taken on a Vertex 70 spectrophotometer (Bruker), with 2 cm^{-1} resolution, in KBr pellets (1 mg of the corresponding sample in 100 mg KBr). The surface morphology of the samples was characterized on high-resolution transmission electron microscope JEOL JEM 2100 operating at an accelerating voltage of 200 kV. The total (O*) and the surface (O_s*) active oxygen content of the as-prepared samples was determined iodometrically [20, 21]. The amount of nickel in the prepared samples was measured by atomic absorption spectroscopy (AAS, Perkin-Elmer).

The process of low temperature (20 – 30°C) catalytic oxidation of HCHO was carried out in a thermostated 400 cm^3 glass reactor under constant stirring. In a typical run, 200 ml 50 mg dm^{-3} 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 cm^3 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 were recorded by two-beam scanning UV-Vis spectrophotometer (Cintra 101). All experiments were conducted in triplicate to ensure the reproducibility of experimental results.

RESULTS AND DISCUSSION

The experimental XRD patterns in Fig. 1 reveal that the as-prepared NiO_x/CeO_2 sample and the support CeO_2 represent a cubic fluorite crystallographic phase of ceria with space group Fm3m (225) (JCPDS 81-0792). There were no additional diffraction peaks in the XRD spectrum of NiOx/CeO_2 although the Ni content in the supported catalyst was close to preparation settings as reveal from the AAS analysis. The absence of distinct reflections of Ni-containing oxide phase could be due to its amorphous character (as found for bulk NiOx), as well as to the formation of highly-dispersed oxide layer on the CeO_2 surface. Moreover, the reflexes of NiOx/CeO_2 were apparently broader and less intense, indicating smaller particle size compared with bare support. It was found that the bulk is amorphous.

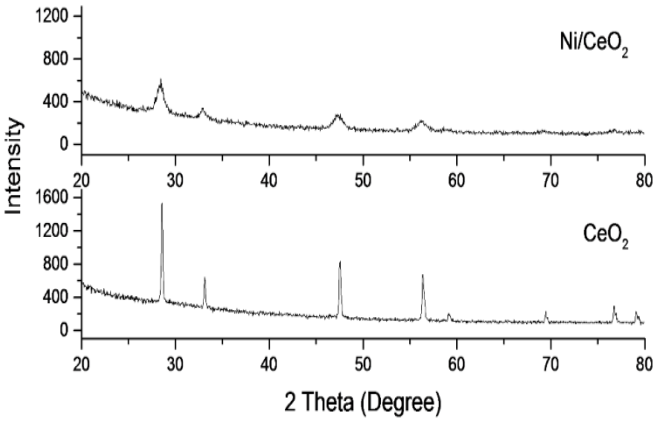

Figure 1. XRD patterns of bulk and CeO_2 supported NiOx

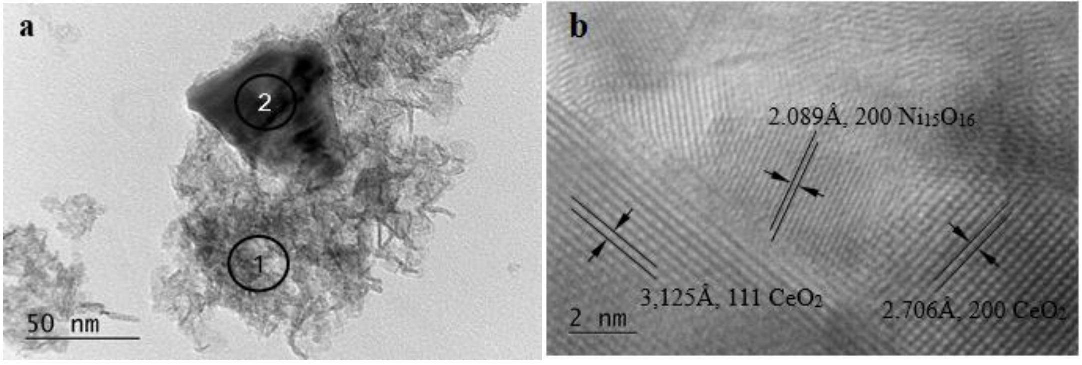

Figure 2. (a) Bright field TEM and (b) HRTEM images of the NiOx/CeO$_2$ catalyst

The presence of NiOx nanoparticles in NiOx/CeO$_2$ was confirmed by TEM and HRTEM (Fig. 2). As observed in Fig. 2a, the NiOx/CeO$_2$ was composed of two types of morphologically-different particles. The first type of particles (No 1 in the image) are elongated, smaller in size and form large aggregates numbering hundreds of particles clustered around the large ones. Indexations of the SAED patterns (not shown) reveal that they correspond to the non-stoichiometric nickel oxide ($Ni_{15}O_{16}$, JCPDS 72-1464). Other particles (No 2), with sizes of about 50 nm are electronically-dense and apparently well faceted. The analysis of the diffraction pattern showed that they consist of CeO$_2$. Well-defined lattice fringes in the HRTEM image of the NiOx/CeO$_2$ sample (Fig. 2b), corresponding to the two types of structures, revealed the existence of a well-crystallized nanoparticles.

The FTIR spectra of bulk and CeO$_2$ supported NiOx catalysts are shown in Fig. 3. A characteristic feature of the both spectra is the presence of a broad and intense band at ca. 573 cm^{-1}, which is due to the stretching vibrations of the surface Ni - O bond and accounts for the presence of active oxygen in the samples. The lower intensity of the band in the IR spectrum of the NiOx/CeO$_2$ indicates the lower content of active oxygen (5.3%) compared with bulk NiOx (8.1%) as confirmed by the chemical analysis. It should be noted that the O_s* of both samples constitutes about 75 % of the total active oxygen. This loosely bonded surface oxygen is a key factor determining high activity of the catalyst in oxidation reactions.

In order to assess the catalytic performance of NiOx/CeO$_2$, series of HCHO oxidation experiment were carried out for comparison. The results of the comparative study of the kinetics of HCHO oxidation in various systems are displayed in Fig. 4. The temporal spectral changes of HCHO in solution during oxidative degradation on NiOx/CeO$_2$ sample are depicted in Fig. 5.

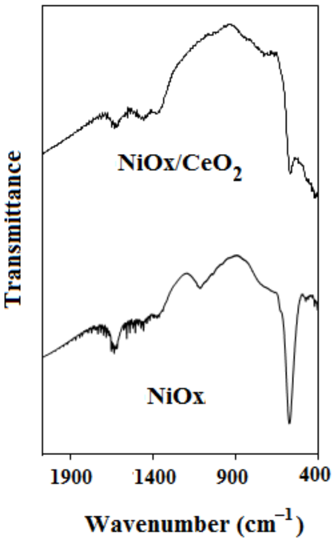

Figure 3. FTIR spectra of bulk NiOx and supported NiOx/CeO$_2$

As can be seen from the presented data, in the absence of catalyst the oxidation of formaldehyde proceeded with low rate – nearly 19% of HCHO is oxidized within 30 min. Evidently, NaOCl itself has limited ability to oxidize organics although it is a strong oxidizing agent. In the presence of unsupported NiO$_x$ but without addition of oxidant (depletive oxidation), the concentration of HCHO decreased only around 37% in the first twenty minutes and was kept unchanged afterwards. Experiments carried out using NiOx/CeO$_2$ alone showed a similar trend with only 7% decrease in final degradation efficiency compared to bulk oxide. Since around 8-fold decrease in the active oxygen content of the catalysts after depletive oxidation was found (confirmed by chemical analysis), it may be speculated that under these conditions HCHO has been oxidized by the O* and, at its depletion, the oxidation process has been stopped. HCHO oxidation over bare CeO$_2$ slightly differs from PMS self-oxidation, implying that pure support did not exhibit catalytic activity in the studied reaction.

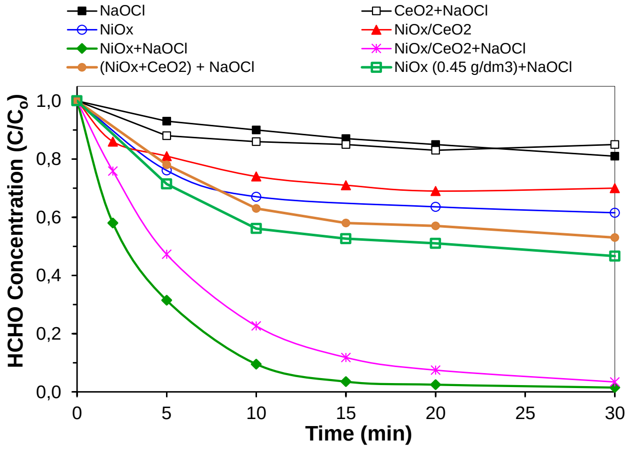

Figure 4. HCHO degradation with time in different systems. Reaction conditions:
50 mg dm^{-3} HCHO, 1.5 g dm^{-3} catalyst loading ,
5 ml dm^{-3} NaOCl, 20◦C.

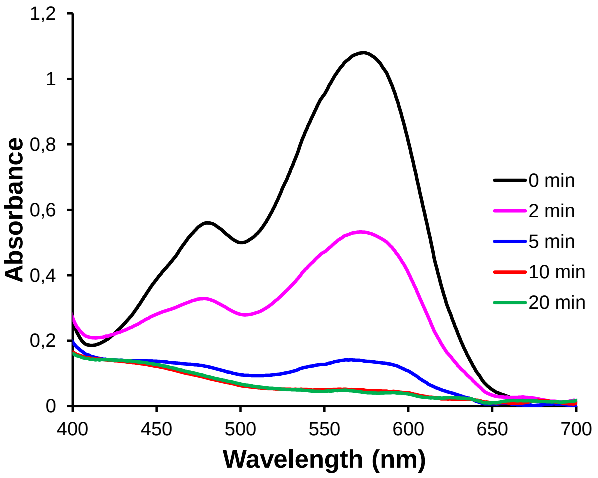

Figure 5. UV–vis spectral changes of HCHO during heterogeneous catalytic oxidation over NiOx/CeO$_2$. Reaction conditions: 50 mg dm^{-3} HCHO, 1.5 g dm^{-3} catalyst loading , 15 ml dm^{-3} NaOCl, 30◦C.

As can be seen from the presented data, in the absence of catalyst the oxidation of formaldehyde proceeded with low rate – nearly 19% of HCHO is oxidized within 30 min. Evidently, NaOCl itself has limited ability to oxidize organics although it is a strong oxidizing agent. In the presence of unsupported NiO$_x$ but without addition of oxidant (depletive oxidation), the concentration of HCHO decreased only around 37% in the first twenty minutes and was kept unchanged afterwards. Experiments carried out using NiOx/CeO$_2$ alone showed a similar trend with only 7% decrease in final degradation efficiency compared to bulk oxide. Since around 8-fold decrease in the active oxygen content of the catalysts after depletive oxidation was found (confirmed by chemical analysis), it may be speculated that under these conditions HCHO has been oxidized by the O* and, at its depletion, the oxidation process has been stopped. HCHO oxidation over bare CeO$_2$ slightly differs from PMS self-oxidation, implying that pure support did not exhibit catalytic activity in the studied reaction.

However, the simultaneous presence of catalyst and oxidant significantly improved the removal rate of HCHO under the similar conditions. More than 96% of HCHO was oxidized within 30 min using NiOx/CeO$_2$. The performance of the supported catalyst was found slightly inferior than that of bulk NiOx although the lower content of the catalytically active phase in the NiOx/CeO$_2$ (30 wt.%). However, when the oxidation was carried out with concentration of NiOx corresponding to its loading on CeO$_2$, there is still 47% of HCHO remaining in the first 30 min. Based on these results it might be concluded that deposition of NiOx on the CeO$_2$ support results in a synergistic effect in catalytic activity. Due to high dispersion of NiOx on CeO$_2$, more amounts of active sites (NiOx) were produced on the NiOx/CeO$_2$ surface than bulk nickel oxide. The synergistic coupling between NiOx and CeO$_2$ in supported sample was also confirmed by the considerably lower catalytic activity of simple physical mixture of NiOx and CeO$_2$.

Under all tested conditions, the HCHO oxidative degradation followed a pseudo first order kinetics confirmed by the linear plots of ln(C_o/C) versus time (Fig. 6). The reaction rate constants (k) and regression coefficients (R^2) of the model fitting are given in Table 1.

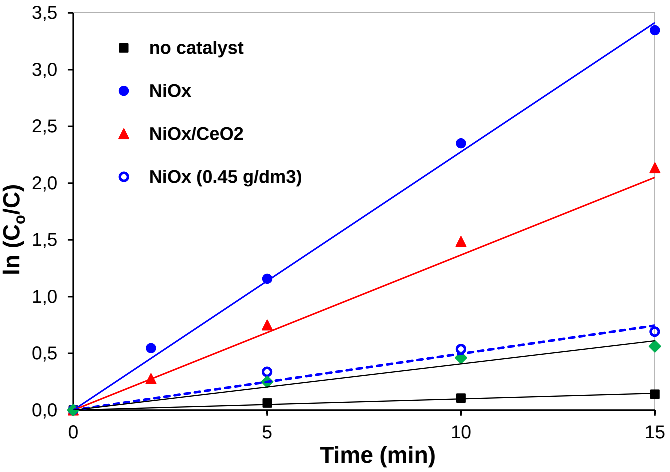

Figure 6. Linear dependences lnC$_o$/C = f (t) (reaction conditions were the same as those indicated in Fig. 4).

Table 1. Pseudo-first order rate constants of the HCHO oxidation process in different systems (1.5 g dm^{-3} catalyst loading , 5 ml dm^{-3} NaOCl, 20°C)

Catalyst	**k (min^{-1})**	**R^2**
No catalyst	0.011	0.982
NiOx	0.227	0.997
NiOx (0.45 g dm^{-3})	0.049	0.982
NiOx/CeO$_2$	0.137	0.991
NiOx+CeO$_2$	0.041	0.986

The optimization of the variables affecting the catalytic oxidation of HCHO in aqueous solutions over NiOx/CeO$_2$ catalyst was carried out following the factorial design of experiments. The variable factors chosen were concentration of catalyst (X_1), concentration of oxidant (X_2), and temperature (X_3). The response measured (Y), through which the effectiveness of the applied method has been assessed, was the degree HCHO degradation in the 10 min from the start of the process (α_{10}, %). Table 2 shows the experimental matrix for the 2^n factorial design (*n* factors, each run at two levels). 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.

Based on the experimental results the following first-order polynomial response equation was obtained, showing the effect of individual variables and interactional effects for HCHO oxidative degradation:

$$Y = 79.91+9.44X_1+8.22X_2 +7.27X_3 + 2.96X_1X_2 - 0.11X_1X_3 - 2.10X_2X_3 - 1.46X_1X_2X_3$$

According to this equation, the studied factors have positive effect on the effectiveness of the catalytic process with the strongest influence being on the amount of the catalyst (Fig.7). The rate constant increased *ca*. 2 times with increasing NiOx/CeO$_2$ concentration from 0.5 g dm^{-3} to 15 0.5 g dm^{-3} with identical other factors due to the availability of more active sites on the catalyst surface for activation of oxidant. Maximum purification effect for shortest time (*ca*. 10 min) was achieved at upper level of the three factors.

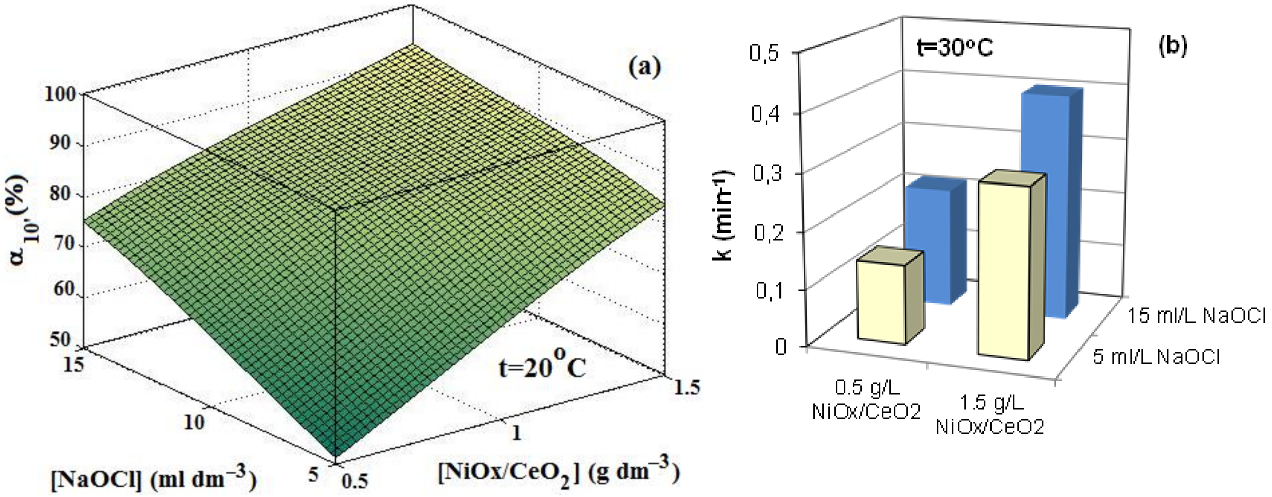

Figure 7. Interaction effect of the studied variable factors on (a) the degree of HCHO catalytic degradation over NiOx/CeO$_2$ and (b) the rate constant.

Table 2. Experimental matrix and results of the factorial design for HCHO catalytic oxidation over NiOx/CeO$_2$

Run	**Variable factors**						**Responce**
	Experimental values			**Codified values**			**Y (%)**
	[NiOx/CeO$_2$] (g dm^{-3})	[NaOCl] (ml dm^{-3})	T (°C)	X_1	X_2	X_3	
1	0.5	5.0	20	–1	–1	–1	51.3
2	1.5	5.0	20	1	–1	–1	73.4
3	0.5	15.0	20	–1	1	–1	74.9
4	1.5	15.0	20	1	1	–1	91.0
5	0.5	5.0	30	–1	–1	1	67.3
6	1.5	5.0	30	1	–1	1	94.8
7	0.5	15.0	30	–1	1	1	88.4
8	1.5	15.0	30	1	1	1	98.2

CONCLUSIONS

In this study, nanosized NiO_x supported on CeO_2 was prepared and its catalytic performance was thoroughly evaluated for oxidative degradation of HCHO in aqueous solutions using NaOCl as oxidant. Characterization data showed that the synthesis procedure led to formation of nanosized non-stoichiometric nickel oxide $Ni_{15}O_{16}$ with high dispersion on the surface of ceria. The as-prepared NiO_x/CeO_2 presented higher efficiency for HCHO degradation than bulk NiOx and mechanical mixture of active phase and support. It might be suggested that a synergistic effect is produced at loading a catalytically active NiO_x phase onto CeO_2. Using 1.5 g dm^{-3} NiOx/CeO_2, conversion rate of more than 98 % has been achieved for 10 minutes at 30°C. Process optimization performed by applying the factorial design showed that the HCHO degradation efficiency and rate are positively influenced on the studied operational parameters, with the strongest effect being of the catalyst amount. The synthesized catalytic system could be regarded as promising heterogeneous catalyst for the degradation of organic pollutants in water.

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КАТАЛИТИЧНО ОКИСЛЕНИЕ НА ФОРМАЛДЕХИД ВЪВ ВОДНИ РАЗТВОРИ ВЪРХУ NiOx/CeO_2

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(Резюме)

Изследвано е каталитичното поведение на NiO_x нанесен върху CeO_2, получен по модифициран утаечно-окислителен метод, в реакция на пълно окисление на формалдехид (HCHO) във водни разтвори. Синтезираният катализатор е охарактеризиран чрез XRD, HRTEM, FTIR и химически анализ. Установено е, че условията на синтезата благоприятстват получаването на наноразмерен нестехиометричен $Ni_{15}O_{16}$, добре диспергиран върху повърхността на CeO_2. NiOx/CeO_2 демонстрира по-висока каталитична активност в сравнение с ненанесения масивен аналог и физична смес от NiOx и CeO_2, което предполага синергичен ефект между активната фаза и носителя. Изследвано е влиянието на основни реакционни параметри като количество на катализатора, температура и концентрация на окислителя върху ефективността на процеса на каталитично окисление на HCHO. Проведен е многофакторен експеримент за оценка влиянието на тези параметри върху ефективността на окислителния процес. Резултатите показват, че оптималните условия за бързо и пълно окисление на HCHO са температура 30°C, количество на катализатора 1.5 g dm^{-3} и концентрация на NaOCl 15 ml dm^{-3}. Синтезираният NiOx/CeO_2 катализатор може успешно да се използва за пречистването на отпадни води, съдържащи формалдехид във високи концентрации.

***Ключови думи**: формалдехид, каталитично окисление, NiO_x/CeO_2; NaOCl*