Study on the catalytic activity of nanosized NiOx for oxidative degradation of 2,4dichlorophenol in aqueous solutions

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

Nanosized NiOx was prepared and tested as heterogeneous catalyst for low-temperature oxidation of 2,4dichlorophenol in aqueous solution using air as an oxidant. The catalyst employed was synthesized by non-conventional ultrasound assisted precipitation-oxidation method with reverse order of precipitation. The physicochemical properties of the as-prepared catalyst were characterized by several techniques, such as XRD, TEM, SAED, FT-IR spectroscopy and chemical analysis. Characterization data reveal that the applied synthesis yields highly dispersed oxide material with a high content of over-stoichiometric active oxygen (O*~8 %), loosely bonded to the surface Ni- ions. The catalyst studied exhibited high activity in degradation of 2,4-dichlorophenol and 100% decomposition could be achieved in short duration of 5 minutes at the optimum conditions, while complete oxidation could be attained in 120 minutes. The effect of several operational parameters, such as catalyst loading, temperature, and pH on the efficiency of the oxidation process was investigated.

Key words: 2,4-dichlorophenol, heterogeneous catalytic oxidation, Ni-oxide system, active oxygen, wastewater treatment

INTRODUCTION

Chlorophenols (CPs) constitute an important group of aromatic compounds which are widely used in the production of pesticides, herbicides, disinfectants and preservatives in wood, dyes, and leather. The large scale production and heavy consumption of CPs generate wastewaters containing these substances at high concentrations. Owing to their high potential of phytotoxicity and zootoxicity, CPs represent one of the most abundant families of industrial environmental pollutants. Chlorophenols could be produced when drinking and industrial waters are disinfected with chlorine but could also be formed as a result of bioaccumulation of compounds with lower molecular weight in natural bodies of water [1-3]. In particular, 2,4-dichlorophenol (2,4-DCP), listed by US EPA as a priority pollutant, is a precursor to the manufacture of the widely used herbicide 2,4dichlorophenoxyacetic acid. It is also the main byproduct of sun induced photolysis of 2,4- dichlorophenoxyacetic acid in soil and water [4]. Due to high toxicity of 2,4-DCP even at low concentrations, resistance for biodegradation as well as its capacity to form organic macromolecules it is

necessary to treat effluents containing chlorophenols prior to its discharge into water [5,6].

At present, the conventional methods used to treat wastewater containing such organic pollutants include biological treatments, adsorption, incineration, air stripping, etc. In general these treatments are inexpensive and safe but have several disadvantages. Biological oxidation can be affected by the toxicity of CPs and requires longer retention time. Non-destructive adsorption method is proven to be effective, however, new secondary waste could be generated that required further treatment and thus increasing the operational cost. Incineration present considerable emission of other hazardous compounds. These essential drawbacks limit considerably practical application of these treatment technologies [7].

Recently, advanced oxidation processes (AOPs) have attracted great scientific and technological interest in the area of water treatment. AOPs are generally based on the production of highly reactive and non-selective hydroxyl radicals through employment of different approaches. These radicals are capable of readily attacking organic contaminants in water, thereby transforming them into harmless end products [8-10]. One of the methods for generation of hydroxyl radical employs photocatalytic processes under exposure of UV light in the presence of semiconductors. The photocatalytic

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activity of nanosized TiO₂ and ZnO for oxidation of 2,4-DCP has been studied "Ba- [11]. The results show that 98% extent of 2,4-DCP oxidation could be achieved for 90 and 60 minutes, respectively, in the presence of these photo-catalysts. The main disadvantage of TiO₂ as a photocatalyst is its inability to absorb visible light that represents 97% of the solar spectrum. This is the reason why scientists have focused their attention on modification of TiO₂ in order to increase its adsorption ability within the visible spectrum.

The photocatalytic activity of TiO_2 modified with porphyrin has been studied in order to evaluate the degree of oxidative destruction of 2,4-DCP under irradiation with visible light. The results indicate that in 4 hours a degree of reduction of the substrate is in the range from 42% to 81% has been achieved when pH=10 [12]. The low level of destruction of toxic substance when visible light is used and the high price of the method when combination with UV light is used limits the possibilities for large scale application of photocatalysis.

An effective and economically feasible process for destruction of a variety of hazardous pollutants in wastewater is based on heterogeneous catalytic reactions providing complete oxidation. Using both suitable catalytic systems and reaction conditions a high selectivity towards environmentally harmless products can be achieved at mild conditions (room temperature and atmospheric pressure).

Our previous studies showed that NiOx is highly effective catalyst for low-temperature oxidative liquid-phase degradation of phenol using air as oxidant. The results obtained show that phenol is completely oxidized for 30 minutes to harmless products - carboxylic acids and CO_2 at ambient temperature and pH 6.0-7.0 [15].

The primary objective of this study is to investigate the effectiveness of Ni-oxide system as heterogeneous catalyst for the oxidative degradation of 2,4-DCP in aqueous solutions. The kinetics of the oxidation process and the effect of various operating parameters influencing 2,4-DCP removal efficiency such as catalyst loading, temperature, and solution pH were studied.

EXPERIMENTAL

Preparation of catalyst

The procedure applied for the synthesis of the catalytic sample was in accordance with the basic requirements to the environmental low-temperature catalysts for complete oxidation in aqueous solution. Some of the typical features of these catalysts include: high dispersity of the catalytically

active phase; high content of active oxygen; high oxidation state and octahedral coordination of metal ions; low binding energy of the M-O bond on the catalyst surface, presence of OH-groups. In order to synthesize the Ni-oxide system complying with these requirements a non-conventional precipitation-oxidation method with reversed order of feeding the precipitator to the system was applied. The synthesis process was assisted by ultrasonic activation using ultrasonic homogenizer UP100H [16]. On the one hand ultrasonic treatment contributes for the more effective homogenization of the reaction mixture and on the other hand it is a prerequisite for the production of nanosized systems with high dispersity and higher specific surface. 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 and allowed to stay in mother liquor for 24 hours. Then it was filtered, washed with distilled water until negative reaction for Cl⁻ and neutral pH, followed by drying at 105°C overnight.

Catalyst characterization

XRD analysis was conducted using X-ray diffractometer TUR-MA 62 equipped with a computerized HZG-3, operated at U = 37kV, Cu K α radiation (λ = 1.5406 Å) and I=20mA. The sample was scanned in the 2 θ =10-80^o range.

The infrared spectra were recorded with a model 1750 Perkin Elmer FT-IR spectrophotometer in KBr tablets (2 mg of the respective sample in 200 mg KBr).

The structural analysis of the samples has been made with high-resolution transmission electron microscope JEOL JEM 2100 at acceleration tension of 200 kV. The two basic operation modes of the microscope have been used namely bright field transmission electron microscopy (BF TEM) and selected area diffraction (SAED).

The chemical analysis of the synthezised catalyst included measurement of the total amount of active oxygen (O^*), represented in both % and g-at.g⁻¹.

Active oxygen is the amount of over-stoichiometric oxygen in the oxide above that correspondding to the lowest stable oxidation state. The total active oxygen content of the catalysts was determined iodometrically. A known amount catalyst 0.1 g \pm 0.001) was added to 25 cm³ dilute (1:10) sulfuric acid containing 2g of potassium iodide in a flask supplied with a ground stopper. After complete dissolution of the sample, the solution is allowed to stand for 10 min and the liberated iodine is titrated with 0.1 N sodium thiosulfate solution 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 Eq. (1) and Eq. (2):

$$O^* = \frac{N \times V \times mgE_{O_2}}{m \times 16}, g - at/g$$
(1)

$$O^* = \frac{N \times V \times mgE_{O_2}}{m} \times 100\%$$
⁽²⁾

where: N – normality of the titrant; V – volume of the consumed titrant solution, cm³; m- catalyst amount, g; $mgE_{O_2} = 0.008$, milligram equiv. O₂.

Catalytic activity test

Heterogeneous catalytic oxidation of 2,4-DCP in aqueous solution was conducted in a thermostated glass reactor of 150 cm^3 capacity at batch mode with constant stirring at around 400 rpm using magnetic stirrer. All experiments followed the following procedure: 100 cm³ 50 mg dm⁻³ aqueous solution of 2,4-DCP was transferred into the reactor and was saturated with air for 20 minutes. Then a fixed amount of catalyst in powder form was added. The reaction was carried out under continuous airflow passing through the system, thus maintainning stationary concentration of oxygen dissolved in water. At given intervals of oxidation process, samples of 4 ml were withdrawn from the suspension, centrifuged at 4000 rpm for 1 min to remove the catalyst and analyzed for residual content of 2,4-DCP and oxidation products.

The reaction progress was followed by UV–Vis spectroscopy and HPLC. The UV-Vis spectra of the samples were recorded from 200 to 500 nm using a UV–Vis double beam spectrophotometer (Cintra 101, GBS, Australia). Due to the very fast catalytic transformation of the substrate (2,4-DCP) in the presence of NiOx, the reaction kinetics was determined by monitoring decrease in absorbance at the maximum wavelength (254 nm) of the intermediate compound produced during the oxidation process.

HPLC analyses were performed using a Knauer Series HPLC system equipped with DAD detector. Separations were carried out by a Purospher Rstar RP-18e column (250 mm \times 4.6 mm i.d.; silica particle size 5 μ m). The mobile phase consisted of acetonitrile mixed with water (v/v; 50:50) at a flow rate of 1 mL/ min; an isocratic elution mode was used. Detection was performed at 254 nm.

pH values of the reaction mixture were measured by digital pH meter (inoLab 740, WTW).

The catalytic activity of the NiOx was evaluated through the degree of conversion of the formed intermediate compound (α , %), calculated according to the Eq. (3) as well as by the rate constant (k, min⁻¹), determined in accordance with a first-order kinetics equation (Eq. 4):

$$\alpha = \frac{A_o - A}{A}.100\tag{3}$$

$$k = \frac{1}{t} \ln \frac{A_o}{A} \tag{4}$$

where A_0 and A are the measured absorptions of the intermediate compound at the moment of its formation and at a any instant time t, respectively.

RESULTS AND DISCUSSION

Powder X-ray diffraction

The XRD measurements of the NiO_x show that the catalyst is X-ray amorphous. The amorphous character of the as-prepared sample determines the chemical and structural isotropy of the active sites centers on the catalytic system surface area which is a prerequisite for high selectivity in the oxidation processes. Although not detectable by the XRD technique, the crystallographic structure of the catalyst was determined through application of TEM and SAED analyses.

TEM and SAED analyses

Fig. 1 shows the typical TEM and the corresponding SAED image of NiO_x , deposited on a carbon coated copper grid. As observed in Fig.1a, the catalyst's nanoparticles have spherical form and diameter in the range 5 nm- 20 nm forming large agglomerates amounting hundreds of particles. The SAED patterns (Fig.1b) obtained from the TEM showed well-defined rings characteristic of the nanocrystalline materials. After the indexation of the diffraction pattern it has been found that they correspond to reflections from non-stochiometric monoclinic Ni₁₅O₁₆ [PDF 72-1464].



Fig. 1. SAED (b) and TEM (a) micrographs of bulk NiOx catalyst.

FT-IR spectroscopy

The FT-IR spectrum of the synthesized catalyst is shown in Fig. 2. Characteristic feature of the spectrum is the presence of wide and intense absorption band located at 573 cm^{-1} . This band is provided by stretching vibrations of the Ni-O bond on the oxide and indicates the presence of active oxygen. Thereupon the intensity of the indicated bands is proportional to the content of O*. The spectral range of appearance of these bands is an evidence for the covalent character of oxygen bonding to the metal ions of the surface, which in its turn justifies the assumption of high activity of the synthesized samples in reactions of complete oxidation.



Fig. 2. IR spectrum of bulk NiOx.

The infrared spectrum of the studied catalytic system show also a broad band with a maximum centered at about 3370 cm⁻¹ (O-H stretching), together with a band at 1630 cm⁻¹ (H-O-H bending). The band at 3370 cm⁻¹ can be ascribed to hydroxyl groups bonded through hydrogen bonds, whereas the band at 1630 cm⁻¹ corresponds to adsorbed molecular water. The inclusion of OH – groups in the composition of the oxide system (as a result of the reverse order of feeding of the precipitator) is

considered appropriate, since they are involved in the oxidation mechanism of the studied process.

Chemical analysis

Data from the chemical analysis of the synthesized oxide system indicated that NiOx is characterized with high total content of active oxygen (5.33%) and about 80% of it is located on the sample surface. This loosely bonded surface oxygen is a key factor determining high activity of the catalyst in complete oxidation reactions.

It should also be noted that the incorporation of over-stoichiometric (i.e. active) oxygen into oxide system is a direct consequence of the applied synthesis method. As a result of the electron transfer between the precursor $Ni(OH)_2$ and the oxygen from NaOCl the oxidation state of metal ions in the oxide system increases and high concentration of ionic oxygen species (O⁻, O⁻₂) on the surface is provided. The latter play a basic role in oxidation catalysis. Most probably the active oxygen is formed as a result of chemosorption of the nascent oxygen (produced on decomposition of NaOCl in strongly alkaline medium) on the precursor surface during the synthesis.

The experimental results obtained from characterization of NiOx give grounds to conclude that the applied synthesis method meets the preliminary requirements described in part 2.1.

Liquid-phase catalytyic oxidation of 2,4-DCP over Ni-oxide system

Initially, in order to assess the contribution of non-catalytic oxidation of 2,4-DCP with air on the overall degree of its degradation a preliminary control test was carried out without adding of catalyst to the reaction mixture. It was found that a negligible destruction of 2,4- DCP occurred with air alone (Fig.3, curve 2). The removal efficiency was less than 1% after reaction for 6 hours, indicating that chemical oxidation of substrate is very slow.

However, the simultaneous presence of NiO_x and oxidant significantly improved the removal rate of 2,4-DCP under the certain conditions. The gradual decrease in 2,4-DCP concentration in the course of oxidation reaction was followed by recording the UV spectra illustrated in Fig.3. It should be underlined that almost complete reduction of the intensity of the absorption band at 286 nm corresponding to the maximum absorption wavelength of 2,4-DCP is achieved in very short duration of about 5 minutes. Considering the negligible parallel removal of contaminant molecules by oxidation with air alone it may be concluded that the very fast destruction of 2,4-DCP under heterogeneous oxidation mode is due to its catalytic transformation.



Fig. 3. UV spectrum profiles of the reaction mixture during chemical oxidation (2) and heterogeneous catalytic oxidation (3) on NiOx; ($C_o = 50 \text{ mg dm}^{-3}$; pH = 6.0, t = 60°C, $C_{cat} = 2 \text{ g dm}^{-3}$).

In the meantime, a new absorbance band at about 254 nm appears at the very beginning of reaction (even at 1 min), but subsequently almost disappears after 120 min, implying that a new structure unit is formed from destruction of 2,4-DCP molecules which further is also complete degraded. The latter is confirmed by results obtained from HPLC analysis.

Fig. 4 shows HPLC chromatograms at 254 nm of 50 mg dm⁻³ 2,4-DCP before and after catalytic oxidation over NiOx. It is evident that as the catalytic reaction occurs, the intensity of 2,4-DCP peak at t_r=10.70 min significantly declined and disappeared after 5 minutes. Simultaneously, a new well resolved peak at t_r=5.87 min is registered, implying generation of one intermediate compound as a result of 2,4-DCP oxidation over NiOx. According to literature reference this peak most likely corresponds to chlorocatechol [17]. Considering very fast catalytic destruction of 2,4-DCP, the kinetic parameters of the oxidation process reaction rate constant (κ ,min⁻¹) and degree of 2,4-DCP conversion $(\alpha, \%)$ were calculated on the basis of the gradual decrease of the intensity of the absorption band of intermediate compound. The linear plot of $\ln(A_0/A)$ versus time confirms the assumed first-order kinetics (not shown).

The influence of the main operational parameters such as pH, amount of the catalyst and temperature on the efficiency and selectivity of the oxidation process were studied.



Fig. 4. HPLC chromatograms of the reaction mixture during heterogeneous oxidation on NiOx; ($C_o = 50 \text{ mg} \text{ dm}^{-3}$; pH = 6.0, t = 60°C, $C_{cat} = 2 \text{ g dm}^{-3}$).

Fig. 5 illustrates the effect of temperature on the effectiveness of 2,4-DCP oxidative degradation. Experiments were carried out at three different temperatures – 25° C, 40° C and 60° C. Results indicate that at 25° C and 40° C an insignificant destruction of the formed intermediate compound is observed even for 120 min, while at temperature of 60° C a complete oxidation is attained within the same reaction period. Therefore, further studies on the influence of pH and catalyst amount on the reaction kinetics were conducted at a constant temperature of 60° C.



Fig. 5. UV spectrum profiles of the reaction mixture during oxidation with NiOx at different reaction temperatures. ($C_0=50 \text{ mg dm}^{-3}$; pH = 6.0, $C_{cat}=2 \text{ g dm}^{-3}$)

Fig. 6 depicts the kinetic curves of catalytic oxidation of 2,4-DCP at 60°C using three different concentrations of NiOx - 0.5 g dm⁻³, 2 g dm⁻³ and 5 g dm⁻³. It was found that four-fold increase in catalyst amount led to complete complete degradation of the intermediate compound in 120 min. Moreover, there is no change in reaction rate constant when the catalyst concentration is increased from 2 g dm⁻³ to 5 g dm⁻³ (Table 1). These results imply that a catalyst concentration of 2 g

dm⁻³ is still enough to achieve complete oxidation of the intermediate absorbing at 254 nm and further incremental addition of the catalyst does not influence the reaction kinetics.



Fig. 6. Effect of catalyst loading on 2,4-DCP degradation. ($C_o = 50 \text{ mg dm}^{-3}$; pH= 6.0; t=60°C).

Table 1. Rate constants of 2,4-DCP oxidation with different catalyst's concentrations. ($C_0 = 50 \text{ mg dm}^{-3}$; pH = 6.0; t = 60°C).

| Catalyst dosage (g dm ⁻³) | First-order rate constants, k.10 ² (min ⁻¹) |
|--|--|
| 0.5 | 0.6 |
| 2.0 | 3.6 |
| 5.0 | 3.8 |

In order to determine the optimal conditions for complete oxidation of 2,4-DCP to harmless products the influence of pH on the efficiency and selectivity of the process was investigated. The results obtained are presented in Fig. 7.



Fig. 7. Effect of pH on the effectiveness of the oxidation process. ($C_o = 50 \text{ mg dm}^{-3}$, $C_{cat} = 2 \text{ g dm}^{-3}$, t=60°C).

It is seen that the higher conversion degree of intermediate compound is achieved when the oxidation process is conducted at pH = 5.0 (α is ~100% in 120 minute). The increase of the alkalinity (with other constant parameters) causes a decrease in the conversion degree and the process is

strongly retarded. At pH = 10.0 only 5% of 2,4-DCP was converted into intermediate for 60 minutes and the latter does not further oxidize. Similar effect of pH was observed during liquid phase oxidation of phenol using the same catalytic system [15] and could be explained by comparing the UV spectra of initial solution of 2,4-DCP at pH=5 and pH=10 (Fig. 8). A batochromic shift of the absorption maximum of 2,4-DCP in alkaline medium is registered which is caused by the formation of phenolate anion characterized with $\lambda_{max} = 303$ nm.



Fig. 8. UV spectrum profiles of the 50 mg dm⁻³ 2,4-DCP initial solutions at pH=5 and pH=10.

Based on these results it could be suggested that the oxidation process is most probably initiated by dissociative adsorption of the substrate on the catalyst surface through tearing of an H atom off from the phenolic OH group. The latter interacts with the active oxygen of the catalyst, thus forming highly reactive surface OH radicals that attack the 2,4-DCP molecule and cause its destruction. The reduced surface of the catalyst becomes reoxidized by oxygen from air continuously bubbled during oxidation. At pH=10.0 2,4-DCP is found mostly in the form of phenolate anion in the solution which makes impossible the formation of OH radicals and respectively the oxidation of substrate. Furthermore, when the oxidation was carried out without bubbling of air in the reaction mixture (depletive oxidation) a different 2,4-DCP degradation profile is observed. Initially, the depletive 2,4-DCP oxidetion occurs as fast as the reaction carried out in the presence of oxygen and then a strong decrease of the oxidation rate with reaction time is observed. Chemical analysis also showed a decrease in the active oxygen content of the catalyst after depletive oxidation experiment (from 5.33% in the fresh NiO_x to 1.09% in used sample). However, the active oxygen content could be completely recovered on the regeneration of the reduced catalyst with NaOCl. These results give us ground to conclude that the catalytic oxidation of 2,4-DCP in an aqueous phase with the participation of NiO_x follows the Mars-van Krevelen oxidation-reduction mechanism. The observed relationship between the amount of Ni-oxide system and the effectiveness of the oxidation process also supports the proposed mechanism of heterogeneous catalytic oxidation, i.e. that the active oxygen of the catalyst takes part in the oxidation process. The larger is the amount of the active oxygen (the mass of the oxide, respecttively), more OH are formed resulting in higher rate of the process.

The long-term stability is an important property for effective catalyst and is crucial for its practical application. To evaluate the stability of the NiO_x catalyst, three rounds of the 2,4-DCP degradation reaction was conducted with the recycling of the catalyst under the same reaction conditions. After the degradation was finished, the catalyst was recovered from the reaction mixture, washed thoroughly with double distilled water and dried overnight before the next run. The recycling test results showed that the catalyst activity remained unaffected in the second round reuse and decreased slightly in the third test whereupon 2,4-DCP removal was still about 90% at 5 minute.

CONCLUSION

Nickel oxide catalyst was prepared by employing non-conventional ultrasound assisted precipitation-oxidation method with reverse order of feeding of the precipitator to the system. The catalytic performance of the as-prepared NiO_x for low-temperature oxidation of 2,4-DCP in aqueous solutions with air was studied. The obtained results show that 2,4-DCP could be completely degraded in aqueous solutions by heterogeneous catalytic oxidation over NiO_x in 120 min at temperature 60°C. The high catalytic activity of the sample is due to the high content of active oxygen and the nano-dimension of the catalyst's particles, resulting from the applied non-conventional synthesis procedure. The effect of the main operating parameters on the reaction kinetics and 2,4-DCP degradation efficiency were investigated as well. The obtained results indicate that 2,4-DCP is completely oxidized to harmless products at temperature 60°C, pH 5.0-6.0. and concentration of the catalyst 2 g dm⁻³. The simple scheme for the synthesis of the Ni-oxide system and its efficiency

for degradation of 2,4-DCP is a prerequisite for its practical application for purification of wastewaters containing toxic organic compounds.

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ИЗСЛЕДВАНЕ НА КАТАЛИТИЧНАТА АКТИВНОСТ НА НАНОРАЗМЕРЕН NiOx ЗА ОКИСЛИТЕЛНА ДЕСТРУКЦИЯ НА 2,4-ДИХЛОРФЕНОЛ ВЪВ ВОДНИ РАЗТВОРИ

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(Резюме)

Синтезиран е наноразмерен NiOx и е проучена каталитичната му активност за нискотемпературно окисление на 2,4-ДХФ във водни разтвори с въздух. За получаването на каталитичния образец беше приложен неконвенционален утаечно-окислителен метод с обратен порядък на утаяване, подпомогнат с ултразвукова активация. Синтезираната по посочения метод наноразмерна каталитична система беше охарактеризирана чрез XRD, FTIR, TEM, SAED и химичен анализ. Данните от охарактеризирането показаха, че приложеният метод за синтез благоприятства получаването на високо дисперсни наноразмерни оксидни материали, характеризиращи се с високо съдържание на силно подвижен свръхстехиометричен активен кислород (О*~8 %). Резултатите от настоящото проучване показват, че изследваният катализатор проявява висока каталитична активност относно окислителната деструкция на 2,4-ДХФ във водни разтвори с въздух. Пълно превръщане на субстрата се постига за реакционен период от 5 мин. при оптималните условия на процеса, а минерализацията и на интермедиата се извършва за реакционен период от 120 мин.. Изследвано е влиянието на основни операционни параметри върху ефективността на процеса- температура, рН и маса на катализатора.