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Alumina-supported nickel oxide for ozone decomposition and catalytic ozonation of CO and VOCs

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Abstract

An alumina-supported nickel oxide system with overstoichiometric oxygen (NiO_x/Al_2O_3) was investigated with respect to heterogeneous catalytic decomposition of ozone, complete oxidation of volatile organic compounds (VOCs) and oxidation of CO. The catalyst was prepared by a deposition oxidation–precipitation method and was characterized by chemical analysis, XPS, XRD, IR techniques, magnetic and adsorption measurements.

The experiments were performed in the temperature range of −50 to 250 °C in an isothermal plug-flow reactor. A very high activity of the catalyst towards ozone decomposition was observed even at temperatures below −45 °C and at the same time the catalyst remained active for a long time. The activity of the catalyst with respect to complete oxidation of VOCs and oxidation of carbon monoxide was studied in presence of different oxidizing agents (ozone or oxygen). A significant increase in catalytic activity and decrease in reaction temperature were observed using ozone as an oxidant. Two main reasons for this behaviour were found: (i) the high content of active and mobile oxygen obtained during the synthesis on the catalyst surface, and (ii) the catalytically active complex of $Ni^{4+}O(OH)_2$, formed during the reaction of ozone decomposition and able to oxidize VOCs at room temperature.

Keywords: Nickel oxide; Ozone decomposition; CO oxidation; VOCs complete oxidation

1. Introduction

Catalytic processes are used for removing harmful components from waste gases. It is important to reduce the temperature of the catalytic reactions with a view to saving energy and at the same time keeping a high catalytic activity. Therefore, investigations are aimed at finding effective low-temperature catalysts or new catalytic processes. Such an appropriate process is ozone catalytic oxidation (OZCO method), which uses ozone as an oxidant in catalytic oxidation reactions. Ozone is known as a strong oxidizing agent for waste and drinking water treatment, sterilization and deodoration [1–3]. During the exploitation of copiers and laser printers, ozone is released into the office air [4]. Due to the fact that ozone itself is toxic, the residual ozone from these processes must be removed. The main method for neutralization of waste gases containing residual ozone is the heterogeneous catalytic decomposition. The catalytic ozonation is a promising method ensuring the purification of waste gases [5–10] and waters [11–13] from organic contaminants. The main hypothesis is that the catalytic ozone decomposition yields a highly reactive oxygen species which could completely oxidize the toxic compounds at lower temperatures [6–10].

Among transition metals oxides, nickel oxides, both unsupported and supported on different oxide support materials (including alumina), belong to the most important catalysts for complete oxidation. They are widely used in various reactions, such as reduction of NO_x [14], oxidation of CO [15–18], partial and complete oxidation reactions of various organic substances [19,20] and in electrocatalysis [21,22]. In previous publications [23] we investigated a higher nickel oxide system, prepared by the oxidation-precipitation method, which contained an overstoichiometric amount of oxygen and Ni ions in a high oxidation state. It has been found that the obtained system, denoted as NiO_x, has a high catalytic activity towards some oxidation reactions taking place in aqueous and in gaseous phase [24–26] as well as in the reaction of ozone decomposition (our unpublished data). According to the results obtained, the synthesized nickel oxide system is prominent and useful in a wide field of appli-

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cations in environmental protection. From a practical point of view it is important to investigate the catalytic properties of this oxide system upon deposition on support materials.

The aim of the present work is to investigate the catalytic activity of an alumina-supported nickel oxide system with overstoichiometric oxygen (denoted as NiO_x/Al_2O_3) during heterogeneous catalytic decomposition of ozone. Based on the high oxygen content in this catalyst, the oxidation of CO and organic substances, using two-different oxidants (ozone and oxygen) will be studied.

2. Experimental

2.1. Sample preparation

The NiO_x/Al_2O_3 catalyst was prepared by a deposition oxidation–precipitation method in an aqueous solution. The active phase of the supported catalyst (NiO_x) was synthesized according to the procedure described in detail in [23]. The procedure applied to the preparation of the supported sample was as follows: the required amount of nickel sulphate was dissolved in 150 ml of deionised water. The solution was heated to 70 °C and then the support (γ-Al_2O_3) was added and kept under continuous stirring for 4 h. After cooling to room temperature, the impregnated catalyst precursor was separated from the solution and added to a mixture of aqueous solutions of NaOH (4 M) and NaOCl (1 M). The solid was kept digested for 24 h, washed several times (until the disappearance of chlorides), then dried in an oven at 110 °C for 12 h.

2.2. Sample characterization

The bulk unsupported NiO_x catalyst was characterized by means of IR, XPS, ESR, DTA, X-ray diffraction and chemical analyses. The specific surface areas of the supported catalyst NiO_x/γ-Al_2O_3 and the γ-Al_2O_3 support were determined by the BET method using low-temperature nitrogen adsorption. Pore size distribution was evaluated from the adsorption curve of the isotherm, using the procedure developed by Orr and Dalla Valle [27]. The chemical composition was determined by atomic absorption spectrometry with Pye Unicam SP90V. The total overstoichiometric oxygen or the so-called active oxygen content, O^* (the active oxygen content is considered to be the amount of oxygen above the stoichiometric content in the oxide, corresponding to the lowest stable valence state [28]) was determined by a direct iodine method [29]. Assuming that all nickel is exposed on the surface of the support, the nickel surface density was calculated. The infrared spectra in the region of 4000–400 cm^{-1} were recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution <2 cm^{-1}) using KBr discs as matrices. X-ray powder diffraction technique (XRD) measurements were carried out using a DRON-3 apparatus with Cu Kα radiation and scintillation calculation. The XPS studies were performed in a VG Escalab II electron spectrometer using Al Kα radiation with energy of 1486.6 eV. The residual gas pressure in the analysis chamber was 10^{-7} Pa. Binding energy values (BE ± 0.2 eV) were referenced to the C 1s line at 285.0 eV as well as to the Al 2p line of the alumina support at 74.3 eV. The integrated peak area of the Ni 2p line was normalized to that of the relevant Al 2p line corrected by the corresponding photoionization cross sections. The accuracy of the measured BE was ±0.2 eV. Magnetic measurements were carried out in air with a magnetic apparatus constructed according to the Faraday method. The magnetic susceptibility (χ) was measured in the temperature range of 290–490 K with a magnetic field intensity varying from 2×10^3 to 10×10^3 Oe. The magnetic moments (BM) were calculated based on the magnetic susceptibility with a correlation of diamagnetic susceptibility of the support and diamagnetic corrections for Ni and O^{2-} ions.

2.3. Catalyst activity measurements

The catalytic activity of the samples was investigated in an isothermal plug flow reactor. The catalyst particle size of 0.3–0.5 mm was chosen taking into account the reactor diameter (6.0 mm) and the volume rate (mean value 22 000 h^{-1}, calculated with respect to the total catalyst bed volume) in order to reduce the effect of external diffusion. The preliminary treatment of the catalysts included heating at 120 °C for 1 h in air flow. The rate of the gas flow was 4.4 l/h, the catalyst volume 0.2 cm^3, and the mass of the catalyst under consideration 0.19 g.

Ozone was synthesized in a flow of oxygen (99.7% dried over silica gel) using an ozone generator with a silent discharge of 4–6 kV between the electrodes. The inlet concentration of ozone for the reaction of ozone decomposition varied between 12.0 and 14.0 g/m^3. The ozone concentration was analyzed with an Ozomat GM (Germany) ozone analyzer with an accuracy of ±0.1 g/m^3. The reaction temperature varied between −50 and 25 °C and was maintained with an accuracy of ±0.2 °C.

The catalytic oxidation of CO and *iso*-propanol were carried out within the range of 22–140 °C and 22–250 °C, respectively. The amounts of CO and *iso*-propanol were dosed by an Ismatex MS2/6 (Switzerland) pump. The oxidizing agent was oxygen from synthetic air (gas mixture of 80% nitrogen and 20% oxygen) or ozone produced in oxygen flow. The inlet concentration of carbon monoxide was 0.2 vol.% and for *iso*-propanol 0.1 vol.%. The inlet concentrations of ozone for CO and *iso*-propanol oxidation were chosen in stoichiometric ratios, considering that only one oxygen atom from the ozone molecule is consumed. The rate of complete oxidation was evaluated by measuring the amount of CO_2 formed during the reaction with a Maihak (NDIR) gas analyser. The CO and CO_2 concentrations were determined with an accuracy of ±2 ppm. The same analyzer measured the oxygen with an accuracy of ±100 ppm.

3. Results and discussion

The results obtained for the bulk unsupported NiO_x catalyst show that the applied method of synthesis yields an amorphous and highly disperse NiO_x phase with non-stationary surface properties, a high content of active oxygen, a high oxidation degree ($Ni^{3+}Ni^{4+}$) and octahedral coordination of the nickel ions [23]. Due to all these attractive properties, one can suppose a high catalytic activity for the supported NiO_x/Al_2O_3 catalyst in

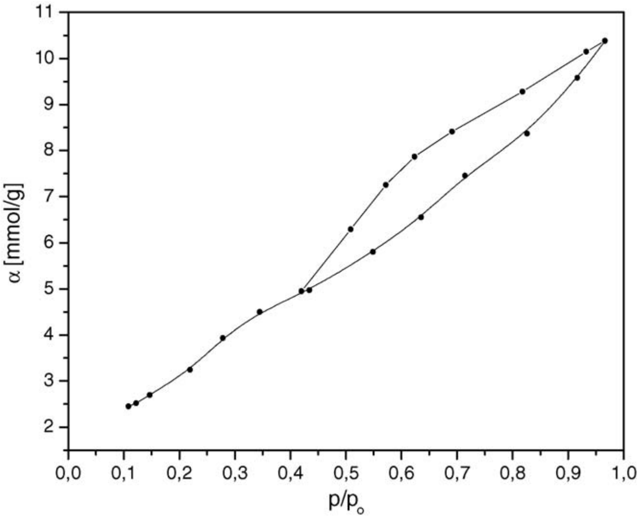

Fig. 1. Adsorption isotherm of $NiO_x/\gamma\text{-}Al_2O_3$ catalyst.

reactions of complete oxidation in the low temperature region. The supported NiO_x/Al_2O_3 catalyst has a larger surface area than does unsupported one and is thus expected to show a higher activity. To check this assumption, the supported NiO_x/Al_2O_3 catalyst was characterized by means of different advanced techniques.

Low-temperature nitrogen adsorption at 77 K was carried out in order to characterize the textural properties of the $NiO_x/\gamma\text{-}Al_2O_3$ catalyst and the $\gamma\text{-}Al_2O_3$ support. The adsorption isotherm, which is IV type according to BDDT classification [30], is presented in Fig. 1. The hysteresis loop is type H3 according to IUPAC classification [31], which indicates that the pores possess "bottle-necked" entrances with different widths. Pore size distribution was evaluated from the adsorption curve of the isotherm, using the procedure developed by Orr and Dalla Valle [27], which assumes cylindrical shape of the pores. Fig. 2 presents the pore size distribution of the NiO_x/Al_2O_3 catalyst, which is typical of mesoporous materials. From Fig. 2 it is evident, that pores with small radii predominate in the sample. The specific surface area of the sample was determined by the B.E.T. method [32] using the adsorption data for the 0.05–0.30 interval of relative pressures. The results of chemical analysis and textural characterization of the supported catalyst are listed in Table 1. The surface area measurements data show that the NiO_x deposition induces a slight decrease of the B.E.T. surface area of the initial support, indicating a partial blockage of the alumina pores with a smaller diameter. The results of the chemical analysis reveal that the deposition of the active phase on $\gamma\text{-}Al_2O_3$ yields nickel oxide with a lower active oxygen content as compared to the unsupported NiO_x system, suggesting some surface reduction of the active phase upon deposition on the support. The XRD analysis shows that the supported catalyst is amorphous.

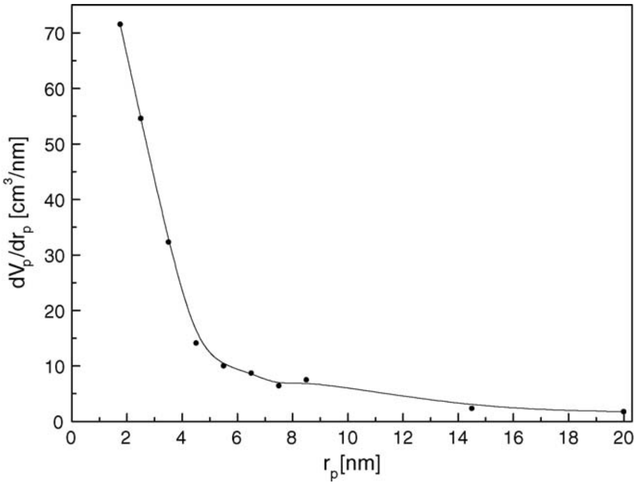

Fig. 2. Pore size distribution of NiO_x/Al_2O_3 catalyst.

Table 1
The results of chemical analysis, magnetic measurement and textural characterization of the supported catalyst

B.E.T surface area of the support (m^2/g)	325
B.E.T surface area of the catalyst (m^2/g)	318
Total pore volume of the catalyst (cm^3/g)	0.34
Ni loading in the catalyst (%, w/w)	8.84
Ni surface density of the catalyst (atoms/nm^2)	3.97
Active oxygen of the bulk NiO_x, O^* (%)	4.4
Active oxygen of the catalyst, O^* (%)	2.9

The magnetic moment $\mu_{\text{eff}} = 3.32$ BM with $\Theta = -46$ was calculated on the basis of the Curie–Weiss equation, with a correlation of $R = 0.9945$. It is known that the magnetic moment of Ni^{2+} ions in an octahedral configuration has a value of 3.54 for $\Delta = 5000\,cm^{-1}$ and does not depend of the temperature (this feature allows the equation of Curie–Weiss to be used). With increasing crystal field, the magnetic moment decreases. The magnetic moment for Ni^{3+} and Ni^{4+} in a strong crystal field is also low. From the foregoing one can conclude that in our case higher oxidation states of the nickel are expected. For the bulk unsupported NiO_x catalyst the magnetic moment is $\mu_{\text{eff}} = 2.75$ with $\Theta = -40$ and $R = 0.9990$. This magnetic moment has a value lower than the theoretic one, because in the bulk catalyst there are more ions in higher oxidation states.

The IR spectra of the $\gamma\text{-}Al_2O_3$ support (a), the bulk phase NiO_x (b), the freshly prepared NiO_x/Al_2O_3 catalyst (c) and the used catalyst after ozone decomposition (d) are presented in Fig. 3. The spectra of (c) and (d) are identical, showing that the catalyst structure is not altered during the catalytic reaction. The broad absorption band having a centre at approximately $3444\,cm^{-1}$ arises from the stretching vibration of hydrogen bonded hydroxyl groups. The absorption band at $1640\,cm^{-1}$ is due to the bending vibration of adsorbed water. These results indicate that all the samples are hydrated/hydroxylated.

An intense absorption band at $570\,cm^{-1}$ is observed in all spectra of (b)–(d) samples. The band at $570\,cm^{-1}$ is not present in the IR spectrum of the pure support (a) and, in accordance with the literature data [33], is assigned to the stretching vibration of the surface nickel–oxygen bond. The band at $570\,cm^{-1}$ also accounts for the presence of active oxygen in the samples, thereupon its intensity is proportional to the content of O^*. The spectral range of its appearance is evidence of the covalent character of the oxygen bonding to the metal ions of the surface, which in its turn justifies the assumption about a high activity of the synthesized sample in reactions of complete oxidation.

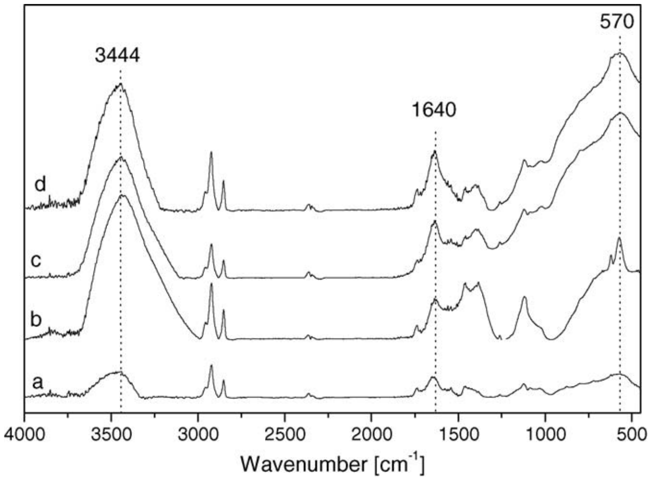

Fig. 3. Infrared spectra of γ-Al_2O_3 support (a), bulk phase NiO_x (b), freshly prepared NiO_x/Al_2O_3 catalyst (c) and worked NiO_x/Al_2O_3 catalyst after ozone decomposition (d).

The XPS spectra of Ni 2p and O 1s core levels of the fresh (curve 1), used in CO oxidation with ozone (curve 2) and in ozone decomposition (curve 3) NiO_x/Al_2O_3 catalysts are presented in Fig. 4a and b. The spectra of all samples show similar features, indicating that upon catalytic reaction there is no significant change in the electronic density of the nickel atoms. A little difference was found for the values of the Ni/Al intensity ratio for fresh and used samples 0.267 and 0.247, respectively. The slight decrease of this ratio for the used sample might be attributed to some agglomeration of the loaded nickel phase. The Ni/O ratio was also found to change: (i) from 0.121 to 0.123 during the oxidation of CO with ozone, this indicating a decrease of the surface oxygen amount; (ii) from 0.121 for the fresh sample to 0.111 for the used one during the ozone decomposition, which reveals an increase of the surface oxygen amount.

The O 1s profiles (Fig. 4a) exhibit a single symmetrical peak centred at 531.4 eV and the main Ni $2p_{3/2}$ peak (Fig. 4b) at 856.4 eV with its shake-up satellite *ca.* 6 eV to higher binding energy. The presence of a prominent satellite structure in the Ni 2p spectra indicates that all the samples investigated are paramagnetic as is also evidenced by the magnetic measurement results. The observed binding energy values of O 1s and Ni 2p components correspond closely to those found for bulk $Ni(OH)_2$ [34], but could also be attributed to O^- and Ni^{3+} ion defects on the surface [35]. The black colour of the catalysts as well as the absence of strong IR absorption at 3650 cm^{-1} arising from the stretching fundamental of nonhydrogen bonded hydroxyl groups (typical of nickel hydroxide) imply that the surface of the samples are not covered with $Ni(OH)_2$. Moreover, in the hydroxide of nickel the 2p shake-up satellite band appears to consist of two components [36]. Considering the fact that the NiO_x/Al_2O_3 catalysts contain an excess of oxygen, this strongly suggests a high concentration of metal-ion vacancies at the surface. Such cation vacancies are known to induce adjacent Ni^{3+} and O^- species [37].

On the basis of the results obtained from chemical analysis, magnetic measurement, XPS and IR techniques it may be concluded that the deposition of NiO_x on the alumina causes a slight decrease in amount of the active surface oxygen and leads to a lower oxidation state of the nickel ions Ni^{2+} and Ni^{3+}.

According to our preliminary tests in reaction of ozone decomposition and oxidation of organic compounds with oxygen, the bulk unsupported system shows very high activity at room temperature. The activity of the NiO_x phase supported on alumina remains unchanged, the supported catalysts having a higher surface area and better mechanic properties than the bulk phase. Fig. 5 depicts the temperature dependence of the catalyst activity towards decomposition of ozone, CO and *iso*-propanol oxidation using two-different oxidation agents: O_3

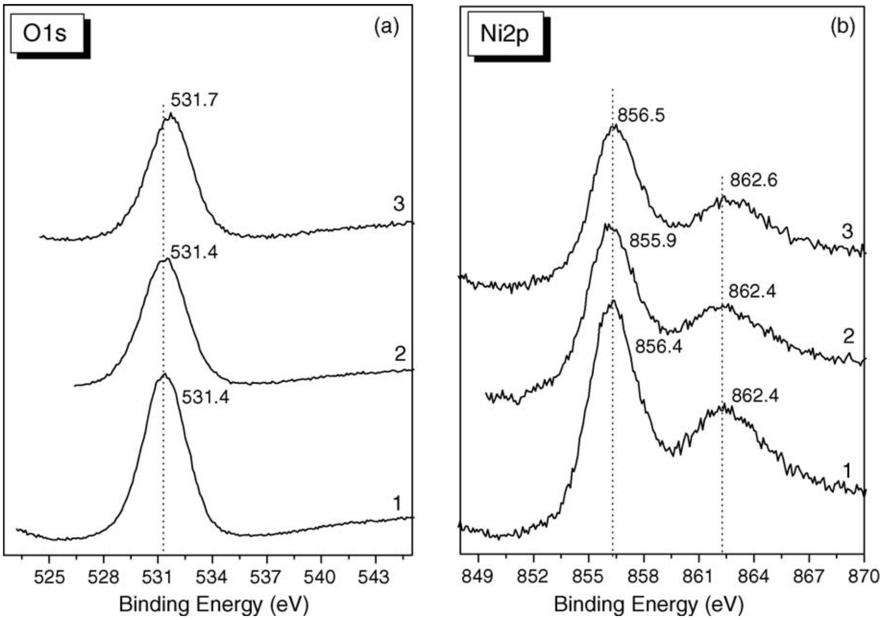

Fig. 4. XPS spectra of NiO_x/Al_2O_3 catalyst: (a) O 1s; (b) Ni 2p. Curve (1) presents a fresh sample, (2) used in reaction of CO oxidation with ozone and (3) used in reaction of ozone decomposition.

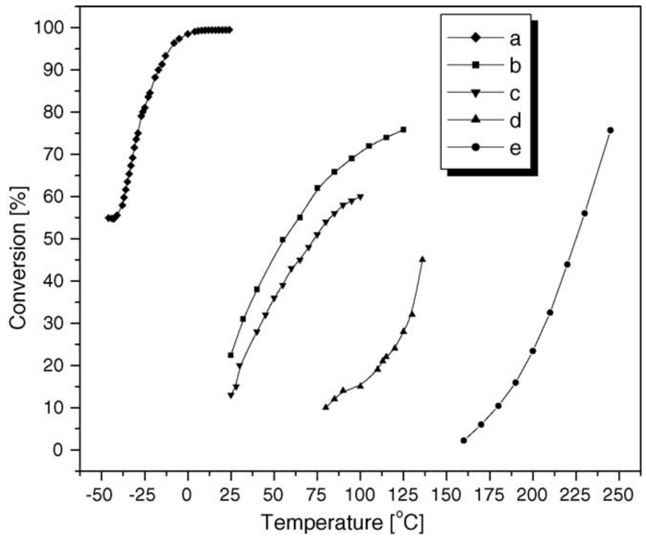

Fig. 5. Conversion-temperature dependences for: (a) ozone decomposition, (b) *i*-propanol complete oxidation with O_3, (c) CO oxidation with O_3, (d) CO oxidation with O_2 and (e) *i*-propanol complete oxidation with O_2 over NiO_x/Al_2O_3 catalyst.

and O_2. It is evident that the activity of the NiO_x/Al_2O_3 catalyst towards ozone decomposition is very high even at low temperature (−50 °C) and reaches almost 100% at room temperature. Fig. 6 presents the time-conversion dependence measured for 550 min at three different temperatures: 0, −20 and −45 °C. As can be seen, the NiO_x/Al_2O_3 catalyst has an extremely high activity at all investigated temperatures and does not show any deactivation during the whole period of catalytic measurements (550 min).

According to earlier investigations [38], the mechanism of catalytic ozone decomposition can be presented as follows:

$$O_3 + Z \rightarrow O^-Z^+ + O_2 \tag{1}$$

$$O_3 + O^-Z^+ \rightarrow 2O_2 + Z \tag{2}$$

$$2O^-Z^+ + O_2 \rightarrow 2Z + 2O_2 \tag{3}$$

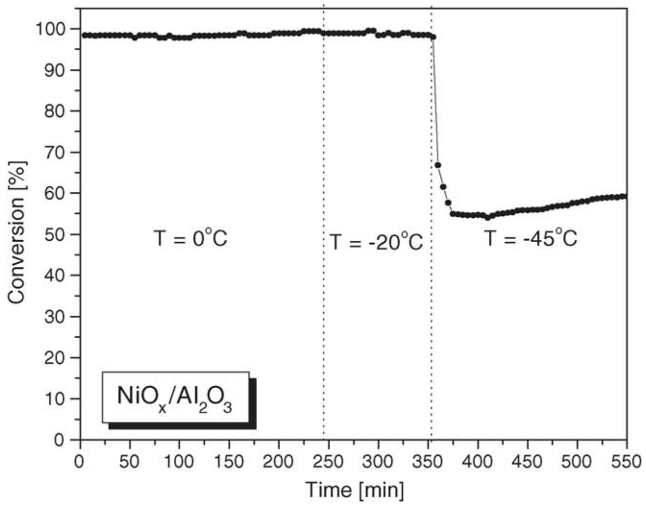

Fig. 6. Conversion-time dependence of the NiO_x/Al_2O_3 catalyst in reaction of ozone decomposition at different temperatures.

$$2O^-Z^+ \rightarrow O_2 + 2Z \tag{4}$$

The proposed mechanism reveals that for a high activity towards ozone decomposition, the catalyst should have active sites (Z) capable to change their oxidation state. Such types of catalysts are the transition metal oxides where several oxidation states are possible.

At room temperature in the presence of ozone, the fresh samples rapidly change their grey-green colour into black, which indicates fast process of oxidation. It is known that preliminary reduced samples, which contain Ni^{2+} ions change their oxidation state into Ni^{4+} in presence of a strong oxidant such as NaOCl [23]. Our opinion is that this process also occurs in ozone containing environment. We assume that the ozone decomposition proceeds through the following reaction steps:

$$Ni^{2+}(OH)_2 + O_3 \rightarrow Ni^{4+}O(OH)_2 + O_2 \tag{5}$$

$$Ni^{4+}O(OH)_2 + O_3 \rightarrow Ni^{2+}(OH)_2 + 2O_2 \tag{6}$$

Reaction (6) regains the initial state of the active sites. The highest oxidation state (4+) of the nickel ions is unstable and the complex $Ni^{4+}O(OH)_2$ decomposes with release of oxygen:

$$2Ni^{4+}O(OH)_2 \rightarrow 2Ni^{2+}(OH)_2 + O_2 \tag{7}$$

$$3Ni^{4+}O(OH)_2 \rightarrow Ni^{2+}(OH)_2 + 2Ni^{3+}O(OH) + H_2O + O_2 \tag{8}$$

After ozone decomposition in the samples there are both Ni^{2+} and Ni^{3+} ions, obtained by reactions (7) and (8). It is expected that Ni ions in 3+ and 4+ oxidation states are very active oxidants. To reveal their oxidative properties, the experiments of oxidation of *iso*-propanol and CO were carried out with two-different oxidants: ozone and oxygen. The conversion-temperature dependences (Fig. 5) show that when ozone is used, better conversion can be achieved and at the same time the oxidation temperature of the different substances significantly decreases. It is evident that the temperature for 50% conversion of *iso*-propanol in presence of ozone is by 170 °C lower as compared to the case of oxidation in air. In the case of CO oxidation at 80 °C in presence of ozone the conversion is 54%, whereas in air at the same temperature only 10% can be achieved. Comparison of the catalytic activity at temperatures higher than 80–85 °C for oxidation reactions with ozone is not correct due to the increased effect of homogeneous ozone decomposition [39].

One can see that with the use of ozone, instead of oxygen as an oxidant, the degree of CO conversion is lower than the oxidation of *i*-propanol at a given temperature. Most probably, this is due to the fact that the oxidation with ozone has a mechanism different from that of the oxidation with oxygen. The active complex for oxidation with ozone is $Ni^{4+}O(OH)_2$ which is formed during the decomposition of ozone:

$$Ni^{4+}O(OH)_2 + R \rightarrow Ni^{2+}(OH)_2 + RO \tag{9}$$

where R is the reducing agent (CO or *iso*-propanol) and RO is the product of the oxidation. This type of active complex is not present on the catalyst surface in the oxidation reaction with oxygen.

Therefore, the oxidation with ozone leads not only to a higher catalytic activity at lower temperatures, but also to a change in selectivity of the reaction. The high catalytic activity using ozone as oxidant permits reaction proceeding in a low-temperature region (below 80 °C) which is extremely important for the catalytic oxidation of toxic volatile organic compounds, because it permits saving energy. A very important feature of the NiO_x/Al_2O_3 catalyst is that it possesses activity toward both ozone decomposition and oxidation with ozone, this leading to removal of the residual ozone from waste gases. Hence, the NiO_x/Al_2O_3 catalyst is very suitable for application in environmental catalysis.

4. Conclusion

- According to the results obtained from chemical analysis, magnetic measurements, XPS and IR techniques, the deposition of NiO_x on alumina causes a slight decrease in amount of active surface oxygen and leads to a lower oxidation state (near to Ni^{3+}) of the nickel ions.
- The NiO_x/Al_2O_3 catalyst shows a very high activity at room temperature in both reactions of ozone decomposition and oxidation with ozone, the catalyst remaining active with the time. The catalytic activity with respect to complete oxidation of *iso*-propanol and oxidation of carbon monoxide in presence of ozone is higher than in presence of oxygen. A significant increase in catalytic activity and decrease in reaction temperature were observed with ozone as an oxidant.
- Two main reasons for the high catalytic activity are found: (i) the high content of active and mobile oxygen obtained during the synthesis on the catalyst surface; (ii) the catalytic active complexes of $Ni^{4+}O(OH)_2$, which are formed during the reaction of ozone decomposition and are able to oxidize VOCs at room temperature.

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