

The study of the applicability of invar nanostructures for the reduction of p-nitrophenyl compounds

D.B. Borgekov^{*,1,2}, M.V. Zdorovets^{1,2,3}, D.I. Shlimas^{1,2},
A.L. Kozlovskiy^{1,2,4}, N.A. Khlebnikov³, E.Yu. Kaniukov⁵

¹L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

²The Institute of Nuclear Physics, Almaty, Kazakhstan

³Ural Federal University, Yekaterinburg, Russia

⁴Kazakh-Russian International University, Aktobe, Kazakhstan

⁵Scientific-Practical Materials Research Centre of National Academy of Sciences of Belarus, Minsk, Belarus

E-mail: borgekov@mail.ru

DOI: 10.29317/ejpfm.2020040209

Received: 30.04.2020 - after revision

The results of the study of the phase composition of iron-nickel nanostructures susceptible to electron irradiation on the catalytic reduction of p-nitrophenyl compounds are presented. In the course of the studies, it was found that the nanostructures irradiated with a dose of 250 kGy, which are characterized by the presence of two phases, with the domination of the FeNi phase, have the highest recovery rate. In this case, nanostructures irradiated with a dose of 250 kGy, which showed the highest catalytic reaction rate, have a fairly short lifetime, which may be due to the rapid degradation of the surface of the nanotubes as a result of the interaction of the catalyst with the medium.

Keywords: nanostructures, catalytic activity, electron irradiation, radiation modification.

Introduction

As a rule, the restoration of inert nitro groups is not possible without the presence of a catalyst, and the use of noble metals for these reactions is not only a resource-consuming process, but also expensive [1-4]. Moreover, unlike noble

nanocatalysts based on platinum, gold or silver, nanostructured catalysts based on base metals such as copper, iron, cobalt, nickel, etc. have a higher productivity and surface selectivity, and the possibility of phase transformations with the formation of oxide phases in the surface layer can significantly increase the productivity of the catalysts [5-8]. The presence of a complex phase structure and a large number of grain boundaries for nanostructures serves as additional catalytic centers that make it possible to accelerate the reduction process, without forming agglomerates, which leads to an increase in the operating life [9, 10]. In turn, catalytic reduction processes can be accelerated using oxide structures with a rather complicated electronic structure and multiphase nanostructures [11-13].

One of the most common catalytic reactions for studying the processes of reduction of nitro groups in the presence of catalysts is the reaction of reduction of toxic p-nitrophenyl compounds to p-aminophenyl compounds, which are safe [14, 15].

The aim of this work is to study the effect of electron-beam modification of iron-nickel nanostructures on the catalytic activity in the reduction reaction.

Experimental part

For the electrochemical synthesis of nanostructures, a two-electrode cell with copper cathodes was used, the distance between which is fixed. The process of formation of nanostructures in polymer templates was controlled using the method of chronoamperometry, which consists in controlling the increase in the current density as the pores of the template matrices are filled. The difference in the applied potentials for deposition was 1.75 V. The iron and nickel salts $\text{FeSO}_4 \times 7\text{H}_2\text{O}$, $\text{NiSO}_4 \times 7\text{H}_2\text{O}$ in a given molar ratio were used as the electrolyte solution. The addition of boric (H_3BO_3) and ascorbic ($\text{C}_6\text{H}_8\text{O}_6$) acids was used to achieve the required solution pH of 3, and also as buffer compounds to accelerate the crystallization of crystallites on the walls of tracks in polymer matrices [14, 15].

The structural properties and phase composition of the synthesized microstructures were modified using an ELV – 4 linear accelerator (Kurchatov, Kazakhstan) by irradiating an irradiation dose of 50-500 kGy with a step of 50 kGy with an energy of 5 MeV [15]. The studied microstructures were irradiated in air. Dose control was carried out using film detectors. According to the calculated data, at given electron energies, their mean free path in a similar material is more than 20 μm , while the length of microstructures is 12 μm .

The study of the effect of the phase composition of iron-nickel nanostructures subject to electron irradiation on the catalytic reduction of p-nitrophenyl compounds in 100 mg of an aqueous solution containing 3 μg of nanostructures, 2 ml of 75% $\text{C}_2\text{H}_5\text{OH}$ and 1 ml of 0.2 sodium borohydride. The catalytic activity was measured using UV spectroscopy by recording UV spectra in the wavelength range of 250-550 nm, with an interval of 5 minutes. The reaction rate was estimated by measuring changes in the intensity of the main spectral line.

Results and discussion

The following samples were selected as test objects for assessing the effect of the phase composition on the catalytic activity of nanostructures: the initial sample is characterized by the presence of two phases FeNi_3 and FeNi , irradiated with a dose of 250 kGy, which is characterized by a predominance of the FeNi phase over the FeNi_3 phase, and the samples irradiated with doses 400 and 500 kGy for which the presence of one phase of the FeNi phase is characteristic. Figure 1 shows the results of a change in the UV spectra of catalytic activity in a time scan for all the studied nanostructures, as well as the reaction scheme for the reduction of p-nitrophenyl compounds to p-aminophenyl compounds.

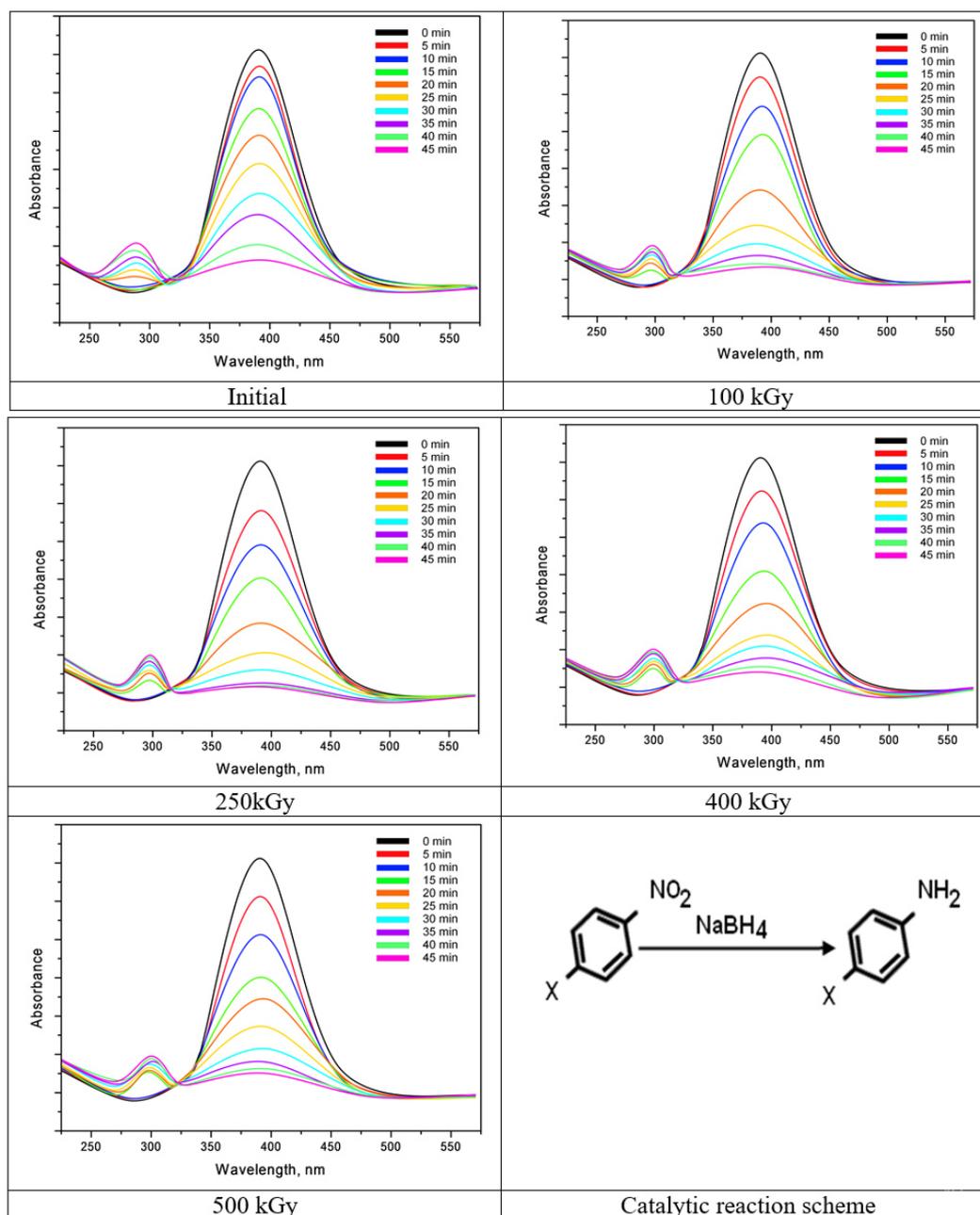


Figure 1. Dynamics of changes in the UV spectra of the studied nanostructures.

As can be seen from the presented data, the characteristic compound of p-

p-nitrophenol is characterized by a spectral maximum at a wavelength of 390-400 nm. In this case, the dynamics of a decrease in the intensity of this maximum characterizes the concentration of p-nitrophenol in the test solution. The appearance of an additional broadened asymmetric maximum in the region of 270-310 nm is characteristic of the group of p-aminophenyl compounds including p-nitrotoluene, p-nitroacetophenone, p-nitrobenzaldehyde, etc. The formation of these compounds and their subsequent accumulation occurs as a result of catalytic reactions. In this case, a decrease in the intensity of the spectral maximum indicates not only a high reaction rate, but also an almost complete reduction of p-nitrophenol to p-aminophenyl compounds, the change of which is shown in the graphs of Figure 2.

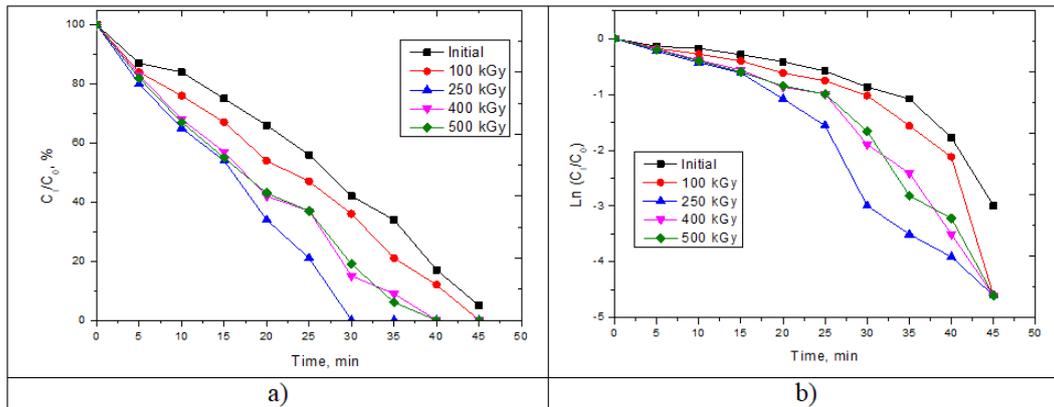


Figure 2. Graphs of the changes in C_I/C_0 (a) and $\text{Ln}C_I/C_0$ (b) reflecting the catalytic activity of the studied nanostructures.

As can be seen from the presented data, the nanostructures irradiated with a dose of 250 kGy, which are characterized by the presence of two phases, with the domination of the FeNi phase, have the highest recovery rate. The presence of two phases increases the reaction rate due to the presence of additional grain boundaries, as well as different electron densities for different phases. Moreover, in the case of irradiated samples with doses of 400-500 kGy, the catalytic reaction rate is practically independent of the radiation dose, which indicates that, at high doses, structural ordering and electron densities achieve a saturation effect. Also, one of the most important characteristics of evaluating the applicability of nanostructures as catalysts is the number of repetition cycles of the reaction during sequential tests. Figure 3 shows the dynamics of changes in the lifetime of the catalysts of the studied nanostructures.

As can be seen from the data presented, the smallest number of repetition cycles is possessed by the initial nanostructures, which are characterized by the presence of a large number of defects and disorders that can have a significant effect on the stability of nanostructures. In this case, nanostructures irradiated with a dose of 250 kGy, which showed the highest catalytic reaction rate, have a fairly short lifetime, which may be due to the rapid degradation of the surface of the nanotubes as a result of the interaction of the catalyst with the medium. At the same time, samples with a high degree of ordering, obtained as a result of irradiation with a dose of 400-500 kGy, have a long resource lifetime of 19-20 cycles of repeatability before degradation of the material. In this case, the decrease

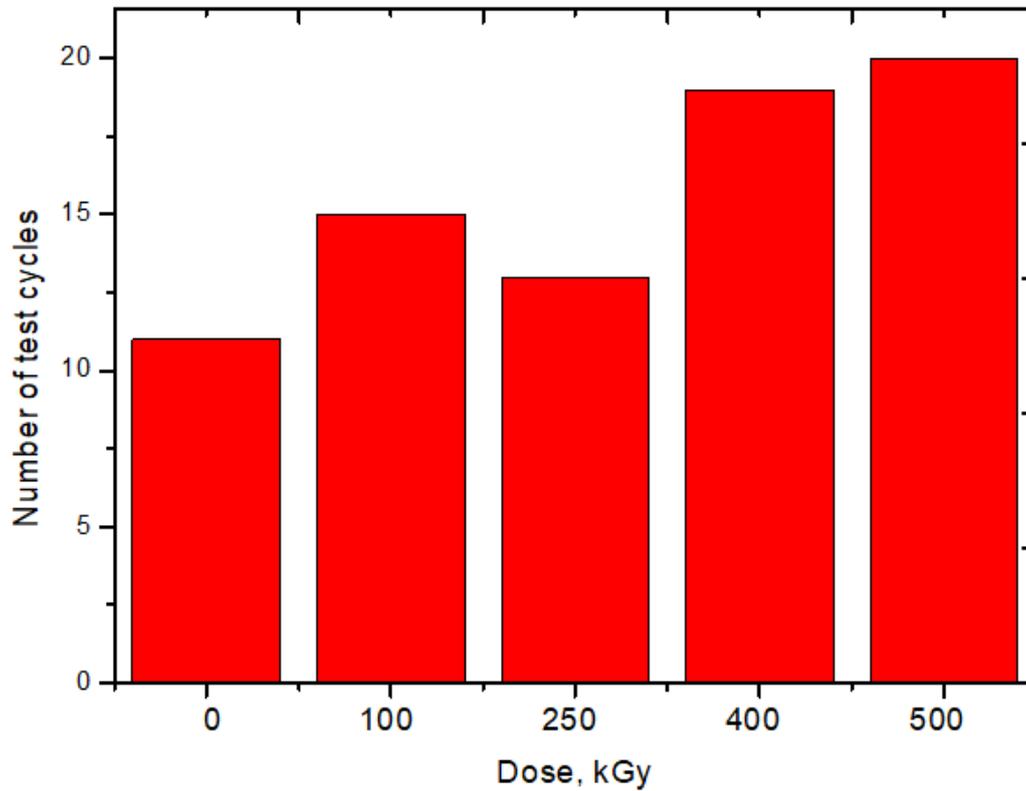


Figure 3. Graph of the number of test cycles for the studied nanostructures.

in the repeatability resource time is caused by the degradation of nanotubes as a result of the formation of impurity inclusions in the surface layer of nanotubes. Figure 4 shows the SEM data of nanotube images after life tests.

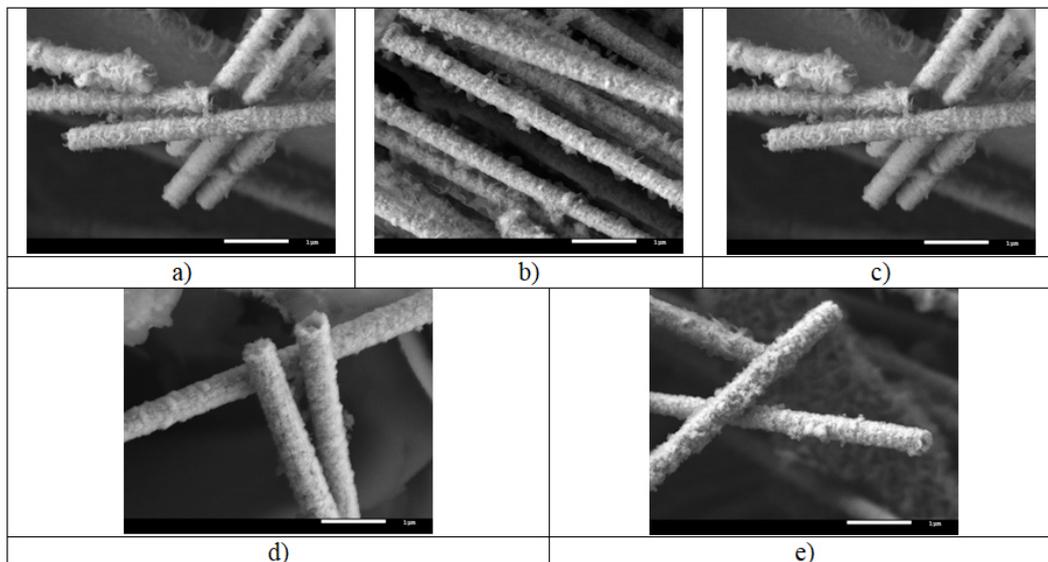


Figure 4. SEM images of nanostructures after catalytic tests: a) initial nanostructures; b) irradiated with a dose of 100 kGy; c) irradiated with a dose of 250 kGy; d) irradiated with a dose of 400 kGy; e) irradiated with a dose of 500 kGy.

As can be seen from the presented SEM images, after catalytic tests, the formation of small growths and impurity inclusions is observed, which are characterized as oxide formations associated with oxidation processes. Moreover, an increase in the radiation dose, leading to structural ordering of nanostructures,

leads to a decrease in the amount of these inclusions on the surface of nanotubes, which indicates a high resistance to oxidation of nanostructures as a result of life tests.

Conclusion

The effect of the phase composition of iron-nickel nanostructures susceptible to electron irradiation on the catalytic reduction of p-nitrophenyl compounds is studied. In the course of the studies, it was found that the nanostructures irradiated with a dose of 250 kGy, which are characterized by the presence of two phases, with the domination of the FeNi phase, have the highest recovery rate. In this case, nanostructures irradiated with a dose of 250 kGy, which showed the highest catalytic reaction rate, have a fairly short lifetime, which may be due to the rapid degradation of the surface of the nanotubes as a result of the interaction of the catalyst with the medium. At the same time, samples with a high degree of ordering, obtained as a result of irradiation with a dose of 400-500 kGy, have a long resource lifetime of 19-20 cycles of repeatability before degradation of the material.

Acknowledgments

This study was funded by the Ministry of Education and Science of the Republic of Kazakhstan (grant AP05133578).

References

- [1] A.E. Shumskaya et al., *Journal of Alloys and Compounds* **810** (2019) 151874.
- [2] A. Kozlovskiy et al., *Materials Research Express* **6.8** (2019) 085074.
- [3] F.E. Osterloh, *Chemical Society Reviews* **42.6** (2013) 2294-2320.
- [4] A. Kozlovskiy, M. Zdorovets, *Materials Research Express* **6.7** (2019) 075066.
- [5] M.J. Kale, *Acs Catalysis* **4.1** (2014) 116-128.
- [6] A. Kolmakov, M. Moskovits, *Annu. Rev. Mater. Res.* **34** (2004) 151-180.
- [7] X. Chen et al., *Chinese Journal of Catalysis* **41.3** (2020) 435-441.
- [8] E.Yu. Kaniukov et al., *Materials Chemistry and Physics* **223** (2019) 88-97.
- [9] J. Deeksha, U.S. Ozkan, *Catalysis* **32** (2020) 44-80.
- [10] D.B. Borgekov et al., *Crystals* **10.4** (2020) 254.
- [11] Antony, Albin, et al., *Physical Chemistry Chemical Physics* **22.7** (2020) 4252-4265.
- [12] G. Rosello-Marquez et al., *Separation and Purification Technology* **238** (2020) 116417.
- [13] A. Kozlovskiy et al., *Ceramics International* **46(8)** (2020) 10262-10269.
- [14] D.B. Borgekov et al., *Surface and Coatings Technology* **389** (2020) 125621.
- [15] D.B. Borgekov et al., *Nanomaterials* **10.1** (2020) 47.