Synthesis of Ni(Co)/Pd Ternary Nanostructures and Their Catalytic Activity in *p*–Nitrophenol Reduction Processes

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Abstract

Ni(Co)/Pd nanosized ternary composite materials have been synthesized by the galvanic replacement method. The structure and phase composition of the obtained Ni(Co)/Pd nanostructures were investigated using SEM, EDX and X–ray powder diffraction. The catalytic activity of the synthesized polymetallic Ni(Co)/Pd nanoparticles was studied using the example of the reduction reaction of *p*–nitrophenol with $NaBH_4$ solution. It was found that in all cases the process of reduction of *p*–nitrophenol $NaBH_4$ in the presence of Ni(Co)/Pd nanoparticles as a catalyst is described by the first-order kinetic equation for *p*–nitrophenol. The catalytic activity of the studied nanoparticles based on nickel (Ni) is varied in the following order: Ni < Ni(Co) < Ni(Pd) < Ni(Co)/Pd. It was shown that the decoration of nanoparticles based on d–elements (Ni, Co) with palladium (Pd) significantly increases of their catalytic activity. Moreover, the reduction rate of *p*–nitrophenol in the presence of Ni(Co)/Pd is almost three times higher, compared to effective catalytic systems known from the references, i. e., such nanosystems can be considered as promising material for the development of new types of magnetically separable catalysts for the production of aminoaromatic compounds.

Keywords: ternary nanoparticles, nickel, cobalt, palladium, catalysis

INTRODUCTION

Bi– and trimetallic nanostructures are promising materials for a wide range of the applications in the chemical industry, in particular in catalysis. The use of such materials in reactions with the participation of hydrogen, in particular in the processes of hydrogen generation (chemical and electrochemical) for hydrogen energy, as well as in the reactions of the reduction of organic substances to practically important products deserve a special attention. Currently, a large number of research groups are engaged in the development of nanoscale catalysts for heterogeneous catalytic processes. An extremely wide range of nanosized mono– and bimetallic catalytic systems for reactions involving hydrogen has been developed and tested, in particular, the electrodes based on nickel nanostructures (Ni_2P) (Liu et al., 2017; Márquez-Montes et al., 2020; Tang et al., 2017), Ni–Co bimetallic nanostructures (G. Wang & Wen, 2018), Ni–Pd (Muthuchamy, Jang, Park, Park, & Park, 2019) Pd–Cr (Yu et al., 2021), etc.; for hydrogen generation

by the hydrolysis of alkaline solutions of sodium borohydride (Kytsya et al., 2022), nanostructured catalysts are used both on the basis of noble metals (Ru, Pt, Pd) (Brack, Dann, & Wijayantha, 2015; F. Wang, Luo, Wang, & Zhu, 2019; Yang, Cheng, Wang, & Cao, 2015), and on the basis of mono– and bimetallic nanostructures of base metals, most often Ni and Co (Guo et al., 2020; Mahpudz, Lim, Inokawa, Kusakabe, & Tomoshige, 2021; Yao, Ding, & Lu, 2020); the catalysts based on noble metal nanoparticles are widely used for the processes of hydrogenation of organic substances (in particular, hydrogennation of nitroaromatic substances with sodium borohydride), namely gold (Au) (Doherty et al., 2019), palladium (Pd) (Aldabergenov, Dauletbekova, Toleutay, Kudaibergenov, & Klivenko, 2017), platinum (Pt) (Li, Wang, Jin, Wang, & Li, 2019), silver (Ag) (Gavade et al., 2016), as well as bimetallic nanosystems Pt–Au (Fu et al., 2014), Au–Ag (Gowthaman, Sinduja, & John, 2016), Pt–Ni (Ghosh, 2004), Pd–Cu (Uozumi & Kobayashi, 2014),

etc. At the same time, taking into account the high cost of nanocatalysts based on noble metals, today there is an increase in the number of publications devoted to the study of the catalytic activity of polymetallic (2 or more components) nanoparticles of various structures, in particular magnetically separable ones based on Ni, Fe and Co (or their oxides), decorated with noble metal nanoclusters. For example, Patra et al., 2017 showed the high activity of Fe_2O_3-based nanostructures decorated with silver nanoclusters (~ 4 nm) as the catalysts for the selective hydrogenation of nitroarenes; trimetallic Ni–Co–Au nanosystems (Jiao et al., 2015), as well as cobalt (Co) nanofibers decorated with gold (Au) or palladium (Pd) nanoclusters, are effective catalysts for obtaining of hydrogen by the sodium borohydride hydrolysis reaction (Zabielaitė et al., 2018) etc. The use of metal nanoparticles based on d–elements as catalysts of chemical processes, in particular in the reactions of the reduction of organic substances to practically important products, has a number of advantages, since the catalysis by such nanoparticles is heterogeneous, which allows the reuse of the catalyst; at the same time, the large surface area of the catalyst and the high activity of metal atoms on the surface of nanoparticles allow to achieve a significant acceleration of the process with a low metal content in the system. In view of the increasingly widespread use of nanocatalysis in chemical transformations, special attention should be paid to the prospects of using of the nanocatalysts for the important reaction of the reduction (hydrogenation) of nitroaromatic substances with an aqueous solution of sodium borohydride in order to obtain industrially important aminoaromatic substances that are widely used in the production of polymers and dyes. On the other hand, when using nanocatalysts, improving the methods of their separation and regeneration remains a problem.

The use of magnetic nanoparticles provides the possibility of combining known procedures of heterogeneous catalysis with the methods of magnetic separation (Shylesh, Schünemann, & Thiel, 2010). Such magnetic separation now successfully using for the removing of pollutants (Rafli, Wahyuni, Zahiro, & Dasna, 2021), magnetite-based nanostructures may be used for the recovery of the noble metals (Qomariyah, Nuryono, & Kunarti, 2021; Rahmayanti, Santosa, Sutarno, & Paweni, 2021)etc. Magnetic separation of the catalyst is cost-effective, as it allows less effort to be spent on filtering and centrifuging the mixture after the reaction. Therefore, an urgent problem is the development of methods of effective immobilization of metal nanocatalysts on the surface of magnetic

media. Taking into account the above mentioned reasons, namely the high catalytic activity of the Ni, Co and Pd in the reactions involving $NaBH_4$ and the ferromagnetic nature of the Ni, Co and their alloys, the aim of this work was to synthesize the ternary magnetically separable nanocatalyst based on Ni-Co alloy decorated with palladium. As a model reaction for the evaluation of the catalytic activity of the catalysts the well-known reaction of p–nitrophenol reduction was chosen (Aditya, Pal, & Pal, 2015).

METHODOLOGY

Materials and Instrumentals

The following reagents were used for the synthesis of metal nanoparticles: nickel acetate $Ni(CH_3COO)_2 \cdot 4H_2O$ (≥99.0%) and cobalt acetate $Co(CH_3COO)_2 \cdot 4H_2O$ (≥99.0%); palladium chloride $PdCl_2$ (≥99.0%). To reduce the metal ions in the synthesis of nanoparticles the hydrazine hydrate $N_2H_4 \cdot H_2O$ (99.0%) was used. Sodium hydroxide (titer standard) served as a pH regulator of the medium during the synthesis of nanoparticles of d–elements. The pH value of the solution was monitored using an Adwa AD1000 ionometer (Hungary). Ethylene glycol (≥99.0%) was distilled at atmospheric pressure and was used as a solvent in the synthesis of metal nanoparticles. The fraction with the distillation temperature 197 ^0C, $n_{D20} = 1,431(1)$ was used for the research.

To study the catalytic activity of the synthesized polymetallic nanoparticles, p–nitrophenol, which was purified by recrystallization in water, was used as a model substrate. Sodium borohydride $NaBH_4$ (≥99.9%) was used without additional purification and was served as the reducing agent of p–nitrophenol.

Methods

Ni(Co)/Pd mono– and polymetallic nanoparticles were separated from the reaction mixture using a neo-dymium magnet and washed with an excess of distilled water. The obtained precipitates were dried in a desiccator under reduced pressure at room temperature.

The shape and size of metal nanoparticles were evaluated using a scanning electron microscope (SEM) EVO–40XVP (Carl Zeiss) with an energy dispersive X–ray microanalysis system INCA Energy 350 (with the option of quantitative analysis of elements in the range from boron to plutonium). The size of the nano-particles was estimated using the AxioVision V 4.8.2.0.

The structure and phase composition of the obta-ined metal nanoparticles were investigated using the X–ray powder diffraction (XRD) using the Aeris–Malvern Panalytical X–ray powder diffractometer
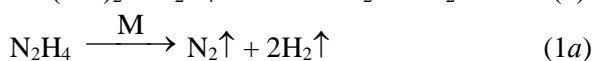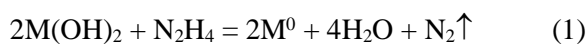
(Cu–Kα radiation, voltage 40 kV, current 15 mA, initial angle 25° (2θ), final angle 100°, step 0.0217). The obtained data were analyzed by full-profile refinement according to the Rietveld method using the WinCSD software package (Akselrud & Grin, 2014).

The study of the kinetics of reduction of *p*–nitrophenol by sodium borohydride in the presence of polymetallic nanocatalysts was carried out at 25 °C in a thermostated reactor equipped with a magnetic stirrer. The concentrations of *p*–nitrophenol and sodium borohydride were 5 mmol/L, the concentration of the nanocatalysts in the all cases was 2 mg/mL. The rate of the reaction was monitored by changes in the absorption spectra of the working solution. For this purpose, the samples with a volume of 0.1 mL were taken at specified intervals, added to 5 mL of distilled water and the absorption spectrum of the solution was recorded in the wavelength range of 190–1100 nm using a single-beam spectrophotometer Uv/mini–1240 (Shimadzu Corp., Kyoto, Japan).

RESULTS AND DISCUSSION

One of the interesting and promising methods of obtaining the polymetallic nanocomposites is the process of galvanic replacement of "passive" metal on the surface of more active metal using the metallic nanoparticles as "sacrificial" materials. In this way, it is possible to obtain the nanostructures in which the properties of the "sacrificial" metal are complemented with the properties of the deposited material. Therefore, in order to obtain ternary nanostructures based on d–element nanoparticles decorated with noble metals, the method of cementation of palladium (Pd) ions with nickel (Ni) and bimetallic Ni(Co) nanoparticles has been studied.

Ni(Co) was synthesized in water / ethylene glycol solutions by reduction of a mixture of corresponding hydroxides with an excess of hydrazine (Kytsya et al., 2022). In general, the reduction of metal ions by hydrazine in an alkaline medium is occurred in accordance with the reaction (1) (Hodges & Pickering, 1966), which is accompanied by the catalytic decomposition of hydrazine (1a, 1b) (Z. Li, Han, & Shen, 2006):

$$2M(OH)_2 + N_2H_4 = 2M^0 + 4H_2O + N_2\uparrow \qquad (1)$$

$$N_2H_4 \xrightarrow{\text{M}} N_2\uparrow + 2H_2\uparrow \qquad (1a)$$

$$3N_2H_4 \xrightarrow{\text{M}} N_2\uparrow + 4NH_3\uparrow \qquad (1b)$$

Ni(Co) was obtained under the following starting conditions: t = 70 ^{0}C; the volume of the reaction medium was 60 mL; the water/ethylene glycol ratio

was 5/1; the total number of ν(Ni + Co) = 2,5 mmol; ν(NaOH) = 50 mmol; ν(N₂H₄) = 200 mmol.

Ni(Co)/Pd was obtained by the method of galvanic replacement in aqueous solutions at 20 °C in a thermostated reactor equipped with a magnetic stirrer without the use of surfactants at pH = 3. The mass of the nanopowder of sacrificial metal (Ni) or Ni(Co) of the composition $Ni_{50}Co_{50}$ was 0,2 g, the volume of the $PdCl_2$ solution was 100 mL. The resulting Ni(Co)/Pd nanostructures were investigated using SEM, EDX and XRD methods.
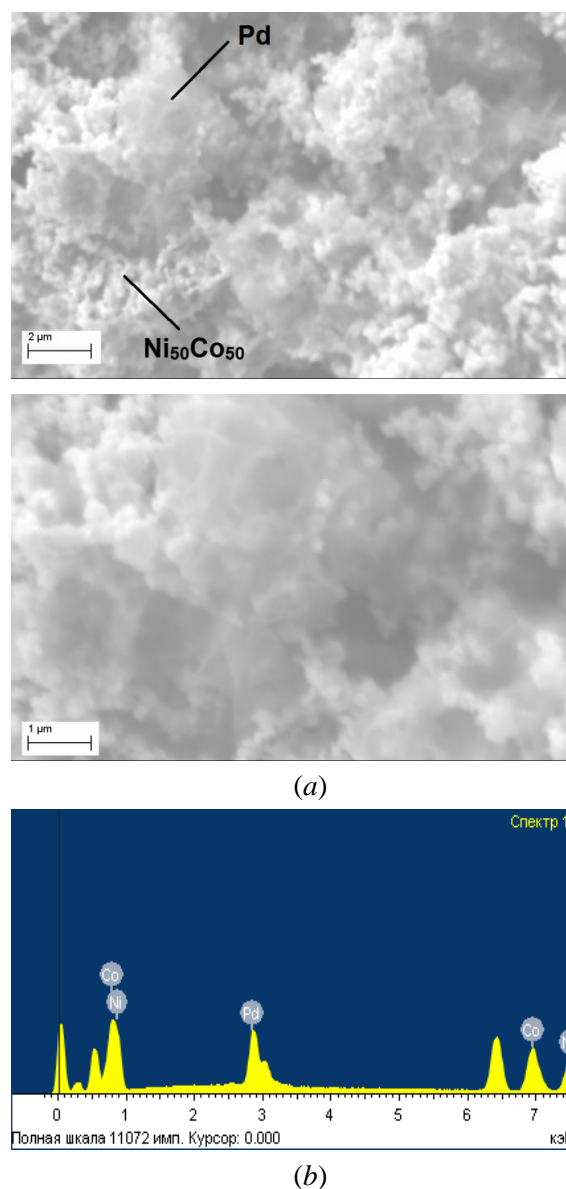

(*a*)

(*b*)

Figure 1. SEM images at different magnifications (*a*) and ED spectrum (*b*) of Ni(Co)/Pd

It was found (Fig. 1, a) that the distribution of palladium in the resulting nanocomposite is uneven,

Table 1. The element composition of the obtained Ni(Co)/Pd

Element	% mass.	% at.
Ni	36.9	41.5
Co	38.4	43.1
Pd	24.7	15.4

namely palladium is crystallized in the form of agglomerates of nanoplates with a thickness of 10–20 nm. It was established (Fig. 1 (b), Table 1) that the element composition of the obtained ternary nanostructures is coincided with the composition of the reaction mixture that indicates the completeness of Pd reduction by Ni(Co) alloy. The analysis of XRD pattern of Ni(Co)/Pd shows that the palladium is crystallized in the form of a cubic phase (space group Fm-3m); any unidentified peaks were not found. The latter fact combined with the results of the element analysis indicates that the obtained nanocomposite do not contain impurities of oxides / hydroxides of nickel or cobalt. At the same time, the presence of anisotropy of peaks was noted for the Pd phase. Such anisotropy, namely the abnormally low intensities of the (200) and (311) reflex peaks compared to (111) and (220) (the latter are indicated by arrows on Fig. 2), may be an indirect confirmation of the formation of lamellar 2D palladium nanostructures in the obtained nanocomposite.
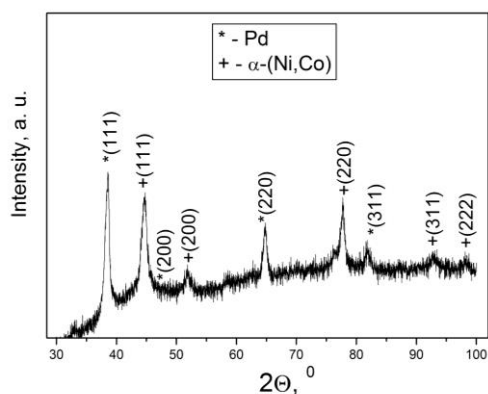

Figure 2. XRD pattern of Ni(Co)/Pd nanocomposite

The catalytic activity of the obtained Ni(Co)/Pd polymetallic nanostructures was investigated using the example of the reduction reaction of p–nitrophenol with sodium borohydride to p–aminophenol, which can be written as a sequence of transformations:
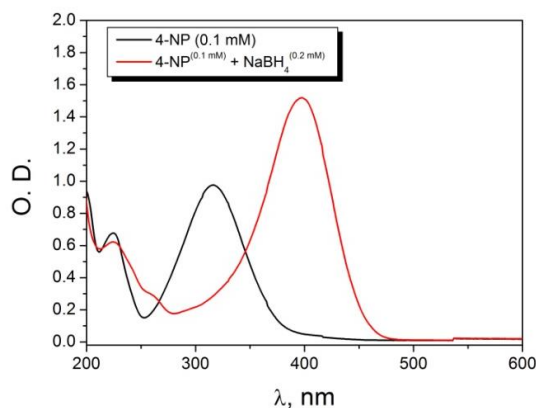
1) formation of p–nitrophenolate anion in the presence of sodium borohydride in the system, which has an alkaline reaction

(2)
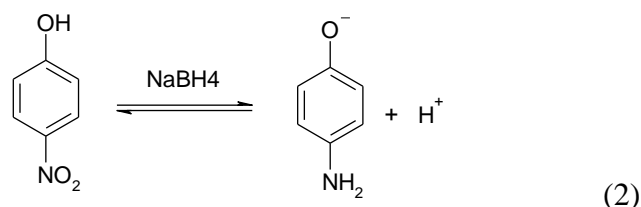
2) interaction of p–nitrophenolate anion with sodium borohydride with the formation of p–aminophenol

(3)
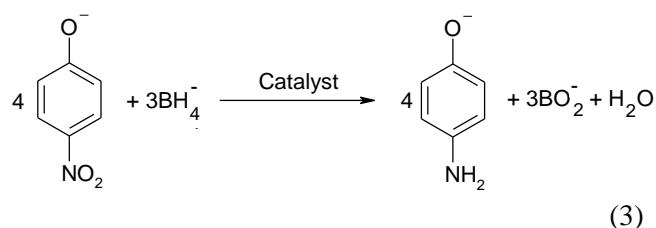
It should be noted that the formation of p–nitrophenolate anion is accompanied by a change in the color of the solution, namely the absorption maximum is increased and is shifted to the long-wave range (from 300 nm to 400 nm, see Fig. 3). Since the p–aminophenol hasn't an absorption maximum at 400 nm, in order to study the kinetics of the reduction reaction of p–nitrophenol with sodium borohydride to p–aminophenol, the method of spectroscopy in the UV–visible range was used.

Figure 3. Absorption spectra of p–nitrophenol and p–nitrophenolate anion

The kinetics of the reduction of p–nitrophenol by sodium borohydride in the presence of Ni, Ni(Co), Ni(Pd) and Ni(Co)/Pd nanoparticles at 25 °C was studied (Figs. 4–7, respectively). The starting concentrations of p–nitrophenol and $NaBH_4$ were 5 mmol/L, the concentration of the catalyst in all cases was 2 mg/mL.
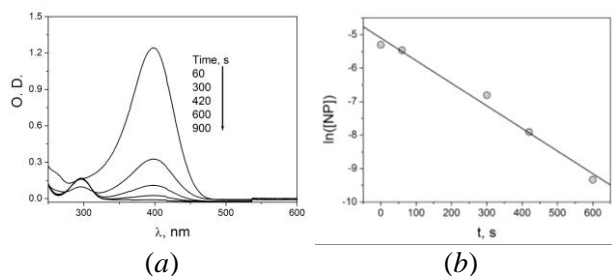
(*a*)   (*b*)

Figure 4. The change of the absorption spectrum of the *p*–nitrophenol solution over time (*a*) and the anamorphosis of the kinetic curve in the coordinates of the first-order reaction (*b*). The catalyst is **Ni** nanoparticles

(*a*)   (*b*)

Figure 5. The change of the absorption spectrum of the *p*–nitrophenol solution over time (*a*) and the anamorphosis of the kinetic curve in the coordinates of the first-order reaction (*b*). The catalyst is **Ni**(**Co**) nanoparticles

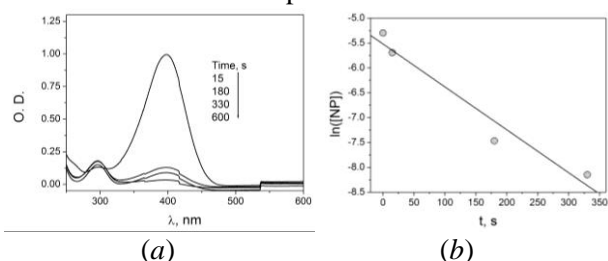(*a*)   (*b*)

Figure 6. The change of the absorption spectrum of the *p*–nitrophenol solution over time (*a*) and the anamorphosis of the kinetic curve in the coordinates of the first-order reaction (*b*). The catalyst is **Ni**(**Pd**) nanoparticles
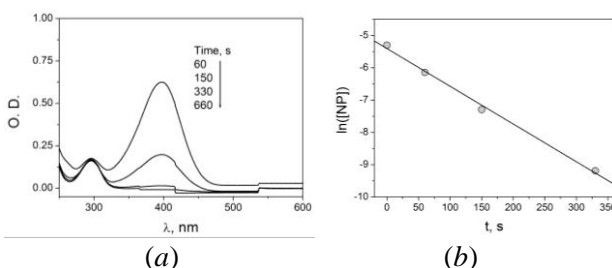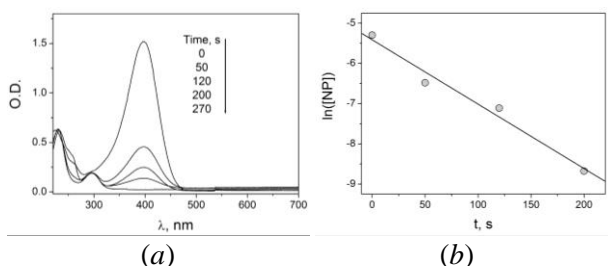

(*a*)   (*b*)

Figure 7. The change of the absorption spectrum of the *p*–nitrophenol solution over time (*a*) and the anamorphosis of the kinetic curve in the coordinates of the first-order reaction (*b*). The catalyst is **Ni**(**Co**)/**Pd**) nanoparticles

It was found that in the all cases such a process is described by the first-order kinetic equation with respect to the concentration of *p*–nitrophenol. Based on the anamorphoses of the kinetic curves of the reduction of *p*–nitrophenol with sodium borohydride in the presence of different nanocatalysts the values of the reaction rate constants were calculated (Table 2).

Table 2. Rate constants of the catalytic reduction of *p*–nitrophenol by sodium borohydride in the presence of Ni, Ni(Co), Ni(Pd) and Ni(Co)/Pd nanoparticles

Catalyst	Catalyst concentration, mg/mL	k, s^{-1}
Ni nanoparticles	2	0.007 ± 0.001
Ni(Co) nanoparticles	2	0.009 ± 0.002
Ni(Pd) nanoparticles	2	0.012 ± 0.002
Ni(Co)/Pd nanoparticles	2	0.016 ± 0.002
Ag/ZnO nanocomposite (Hunge et al., 2022)	2	0.006
Pd nanoparticles (Subhan et al., 2020)	0.8	0.008

As can be seen from the data given in the Table 2, the catalytic activity of the studied nanoparticles based on nickel (**Ni**) is varied in the following order: **Ni** < **Ni**(**Co**) < **Ni**(**Pd**) < **Ni**(**Co**)/**Pd**, and the decoration of nanoparticles based on d–elements (**Ni**, **Co**) with palladium (**Pd**) significantly increases their catalytic activity. Moreover, the reduction rate of *p*–nitrophenol in the presence of **Ni**(**Co**)/**Pd** is almost three times higher compared to the known effective catalytic systems (Hunge, Yadav, Kang, & Kim, 2022) and close to the monometallic palladium nanoparticles supported on the mesoporous silica (Subhan, Aslam, Yan, & Yaseen, 2020). That is, such nanosystems can be considered as a promising material for the development of new types of magnetically separable catalysts for the nitroarenes reduction.

CONCLUSION

The use of metal nanoparticles based on d–elements as catalysts of chemical processes, particularly in the reactions of reduction of organic substances to practically important products, allows achieve a significant acceleration of the process at a low metal content in the system. By galvanic replacement of a "passive" metal on the surface of more active metal using metal nanoparticles as "sacrificial" materials, it is possible to obtain the nanostructures in which the properties of the "sacrificial" metal are complemented by the properties of the deposited material. The results of the study of the catalytic activity of the obtained Ni(Co)/Pd ternary nanostructures on example of the reduction reaction of p–nitrophenol with sodium borohydride to p–aminophenol showed that such systems are a promising material for the development of new types of magnetically separable catalysts for the production of aminoaromatic compounds.

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