

PRIMENA MEHANOHEMIJE U SINTEZI EKOLOŠKE I ODRŽIVE KATALIZE

APPLICATION OF MECHANOCHEMISTRY IN SYNTHESIS OF ECO-FRIENDLY AND SUSTAINABLE CATALYSTS

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Primena mehanohemije u sintezi naprednih materijala i heterogenih katalizatora veliko je i stalno rastuće polje istraživanja i inovacija. Istraživačke aktivnosti fokusirane su na razvoj novih koncepta za projektovanje metoda za pripremu i aktivaciju katalizatora bez otpada i za uštedu energije uz značajno poboljšanje prinosa i selektivnosti proizvoda. Poboljšanje punog životnog ciklusa materijala dobijenih katalizatora zajedno sa boljom reciklažom, ponovnom upotrebom i popravkom vrednih materijala otvorena su područja za nove ideje, naučne i inovativne projekte. Mehanohemijska aktivacija ima značajan uticaj na fizičko-hemijska i katalitička svojstva heterogenih katalizatora kroz uvođenje mehanički izazvanih defekata u čvrstom stanju. Zbog toga se mehanohemijski tretman može uspešno koristiti kao moćno oruđe za pripremu materijala sa projektovanim katalitičkim ponašanjem menjajući njihovu katalitičku aktivnost i selektivnost. Hemijske transformacije izazvane mehaničkim silama u čvrstom materijalu su značajne jer vode do sinteze kojima su obično potrebne visoke temperature i pritisci, što omogućava pripremu novih metastabilnih faza i materijala. Reakcije koje katalizuju mehanohemijski pripremljeni katalizatori mogu se značajno razlikovati u smislu selektivnosti, efikasnosti ili čak reakcionih puteva u odnosu na njihove analoge, reakcije katalizovane tradicionalnim katalizatorima ili nekatalizovanim procesima. U radu su sumirani rezultati naših istraživanja i uspešni primeri visokih performansi mehanohemijski sintetizovane katalize registrovane u probnim katalitičkim reakcijama prečišćavanja izduvnih gasova i vode. Predstavljeni primjeri uključuju potpune reakcije oksidacije isparljivih organskih komponenti i remdijaciju otpadnih voda iz tekstilne industrije. Takođe će biti reči o katalitičkim reakcijama koje se dešavaju u uslovima mehanohemijske aktivacije.

Ključne reči: Mehanohemija, napredni materijali, ekološka sinteza, karakterizacija, održivost.

Application of Mechanochemistry in synthesis of advanced materials and heterogeneous catalysts is a large and continuously growing field of research and innovations. The research activities are focused on the development of new concepts for design of a waste-less and energy-saving methods of catalyst preparation and activation with a significant improvement of the product yield and selectivity. Mechanochemical activation has a significant impact on the physical-chemical and catalytic properties of heterogeneous catalysts throughout the introduction of mechanically induced defects in the solid state. Therefore mechanochemical treatment can be successfully used as a powerful tool for preparation of materials with designed catalytic behaviour changing both their catalytic activity and selectivity. Chemical transformations induced by mechanical forces in the solid are significant since they lead to syntheses that normally need high temperatures and pressures thus allowing the preparation of new metastable phases and materials. The reactions catalyzed by mechanochemically prepared catalysts can be significantly different in terms of selectivity, efficiency or even reaction pathways compared with their counterparts, reactions catalyzed by traditional catalysts.

Key words: Mechanochemistry; Nanosized ferrite materials; Catalysts; Material Characterization; Water purification.

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1 Introduction

Nowadays, transition metal spinel oxides are widely used as magnetic materials, semiconductors, pigments etc. It is well established that various binary and ternary spinel ferrites are effective catalysts for a number of industrial processes such as oxidative dehydration of hydrocarbons, decomposition of alcohols and hydrogen, peroxide, purification of automotive exhaust gases, oxidation of CO and volatile organic compounds (VOCs), as well as PROX reactions [1-2]. It is also confirmed that the physical-chemical properties and catalytic behaviour of spinel oxides depend not only on the nature and the oxidative state of the transition metal ions but also on their distribution in the spinel structure [3-7]. The role of the preparation method and treatment conditions on the morphological and structural features of the ferrites is largely discussed [3, 8, 9]. Large scale application of ferrites with small particles and tailoring of specific properties have prompted the development of widely used chemical methods, including sonochemical reactions [10], sol-gel methods [11], microwave plasma [12], host template [13], co-precipitation [14], mechanical alloying [15], etc. for the fabrication of stoichiometric and chemically pure spinel ferrites nanoparticles. Among these techniques, mechanochemistry is an attractive technique for synthesizing inorganic solids since in addition to producing nanometer grain size particles it can induce chemical and structural transformations in the as-prepared compounds [2, 6, 9]. The present paper studies the synthesis of nanosized nickel ferrites by co-precipitation method and additional mechanochemical or thermal treatment of as-prepared materials. Special attention is paid to the effects of the synthesis method on their catalytic behavior in water purification reactions.

2 Results

Mechanochemistry is based on the proceeding of chemical reactions, which are induced by the input of mechanical energy. It is provided in the material during grinding and leads to numerous effects on an extended crystalline solid such as generation of new interfaces and crystal defects (e.g. dislocations and vacancies), heating, change of particle size and shape, mass transfer, material amorphization, formation of metastable phases. In order to obtain the appropriate conditions of mechanochemical activation and to offer an original technological solution for the preparation of spinel material with enhanced catalytic reactivity and a highly disperse structure, a large number of synthesis conditions were investigated. The effects observed during mechanochemical activation of a solid presuppose quasi-adiabatic accumulation of energy under the single events of sufficient intensity. This means that the accumulation and transfer of energy achieved by mechanical forces depend on numerous factors and milling parameters. The milling energy and intensity were varied by change of milling parameters as milling time, ball to powder weight ratio, milling reactors, etc. So, the great value of the ratio (ball load mass) to the mass of the activated mixture will ensure a high value of activation energy, i.e. high energy acceleration. The milling process gives rise to fragmentation of the matter and the formation of reactive interfaces. Activation time was also varied within a wide range (from 1 to 10 hours).

The optimal synthesis conditions were found in this study and iron-containing nanosized spinel materials with chemical composition $\text{Me}_x\text{Fe}_{2-x}\text{O}_4$ (Me=Ni, Co, $0 \leq x \leq 1$) were prepared. The synthesis was performed in two steps: (1) co-precipitation and (2) thermal treatment or mechanical milling of co-precipitated material. The used starting materials were $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH. At the second step of investigation, the as-obtained powders were additionally treated by one of the following techniques:

- thermal treatment at low temperature (300 °C) at an inert atmosphere;
- mechanical milling by a Retsch Planetary ball mill PM100, Germany in a steel vial together with steel grinding balls with a diameter of 10 mm. The ball-to-powder mass charge ratio was 30:1. The powders were milled for 3 hours at an inert atmosphere.

The precursors and prepared materials were studied at each step of their treatment by numerous physical-chemical methods. X-ray diffraction (XRD) patterns are registered using TUR M62 diffractometer with $\text{Co K}\alpha$ radiation and data interpretation was carried out using JCPDS database [JCPDS-International Centre for Diffraction Data]. Transmission Moessbauer spectra were obtained at room

(RT) and liquid nitrogen temperatures (LNT) with a Wissel electromechanical Moessbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A $^{57}\text{Co}/\text{Cr}$ (activity ≈ 30 mCi) source and an $\alpha\text{-Fe}$ standard were used. The experimentally obtained Moessbauer spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H_{eff}) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined.

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The registered X-ray diffraction patterns of as-prepared samples revealed that the synthesised materials are X-ray amorphous after the first step of their co-precipitation, as well as after additional mechanochemical treatment. It was obtained a complete disappearance of initial compounds reflections ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, the patterns are not shown). There are no data for the presence of any spurious phases in the course of treatment, as well as in the obtained products. Thermal treatment of the co-precipitated material at low temperature leads to a partial increase of material crystallinity and spinel structure was registered as it can be seen on Fig. 1 in case of $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ material. The prepared spinel structure has broad and low intensive reflections. The line shape broadening of pattern indicates low crystallinity degree and high dispersion of the sample. The value of about 15 nm was calculated by Scherrer equation [16] for the spinels particle size of the obtained ferrite sample in this case.

On the other hand, the Moessbauer study of the samples reveals the synthesis of spinel structure after the first step of co-precipitation process. The registered Moessbauer spectra at room temperature (RT) include only superposition of doublet lines. However, with a temperature decrease to the liquid nitrogen temperature (LNT) these doublet spectra become partially splitted into sextet ones. Fig. 2 shows the LNT Moessbauer spectra of co-precipitated $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ material (Fig. 2a), as well as the same material after thermal treatment (Fig. 2b) and after mechanochemical treatment (Fig. 2c). The optimal fit of the spectra and the calculated hyperfine parameter values of the respective components are characteristic for the presence of iron cations in the spinel lattice [17]. The doublet part of the spectra could be regarded to existence of ultradisperse iron oxide particles with nano-metric size ($D < 10$ nm) and superparamagnetic (SPM) behaviour [1, 5, 8]. The sextet part of spectra can be attributed to so-called collective magnetic excitation (CME) behaviour of small particles ($D < 30\text{nm}$) [1, 5, 8]. So, in both cases relaxation phenomena were registered due to the small nanometric particle size of synthesised materials.

The obtained IR data (not shown) also confirm these observations by indicating the typical IR spectra of nickel-ferrite oxides [4, 9].

The registered photocatalytic behavior of synthesized materials in water purification reactions clearly shows the role of mechanochemical treatment for improvement of their dye degradation ability. Comparison of the obtained apparent rate constants in complete degradation of Malachite green oxalate gives the following results:

- photocatalytic activity of as-precipitated sample $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is $9.3 \cdot 10^{-3} \text{ min}^{-1}$;
- photocatalytic activity decreases as a result of thermal treatment of $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ material to the value of $6.0 \cdot 10^{-3} \text{ min}^{-1}$;

- photocatalytic activity of mechanochemically activated $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ sample significantly increases to the rate constant with a value of $13.5 \cdot 10^{-3} \text{ min}^{-1}$. This value is even higher than the photocatalytic activity of the standard UV-light catalyst Degussa P25 ($12 \cdot 10^{-3} \text{ min}^{-1}$), which is also registered for comparison.

3 Conclusions

Mechanochemistry is an emerging method for the preparation of new and advanced catalytic materials with enhanced properties and highly disperse structure. The synthesized materials can be successfully applied in the area of environmental catalysis and, in particular, for wastewater treatment utilizing mixed iron oxide-based materials. An easy and environmentally friendly way to synthesize iron–nickel oxide materials with nanometric particle size was shown in this study. High performance of mechanochemically activated materials was obtained in test photocatalytic reactions of water purification. The presented example includes the complete remediation of wastewaters from the textile industry.

4 Figures

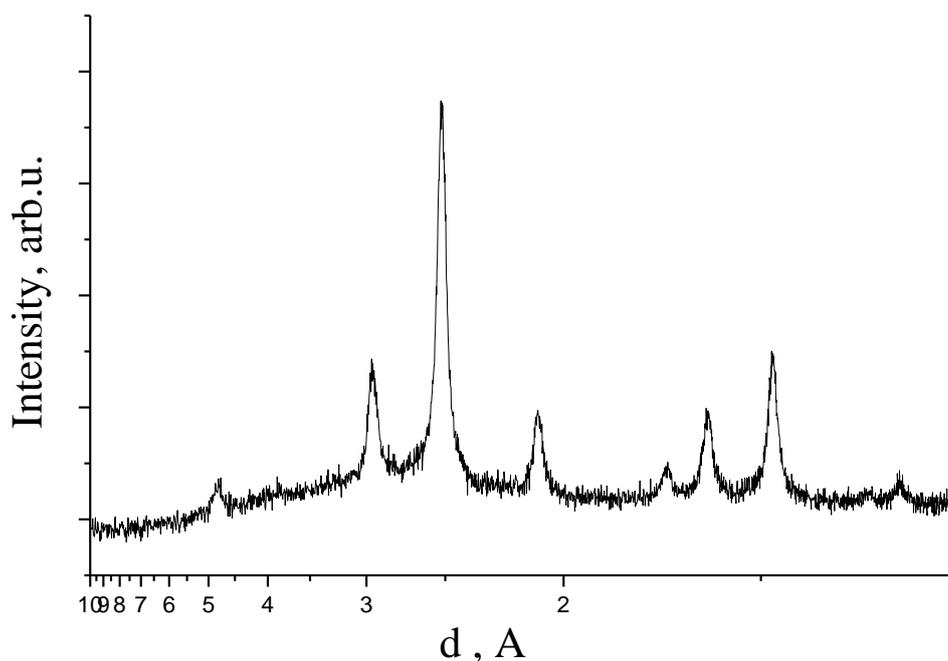


Figure 1. XRD of thermally treated $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ material.

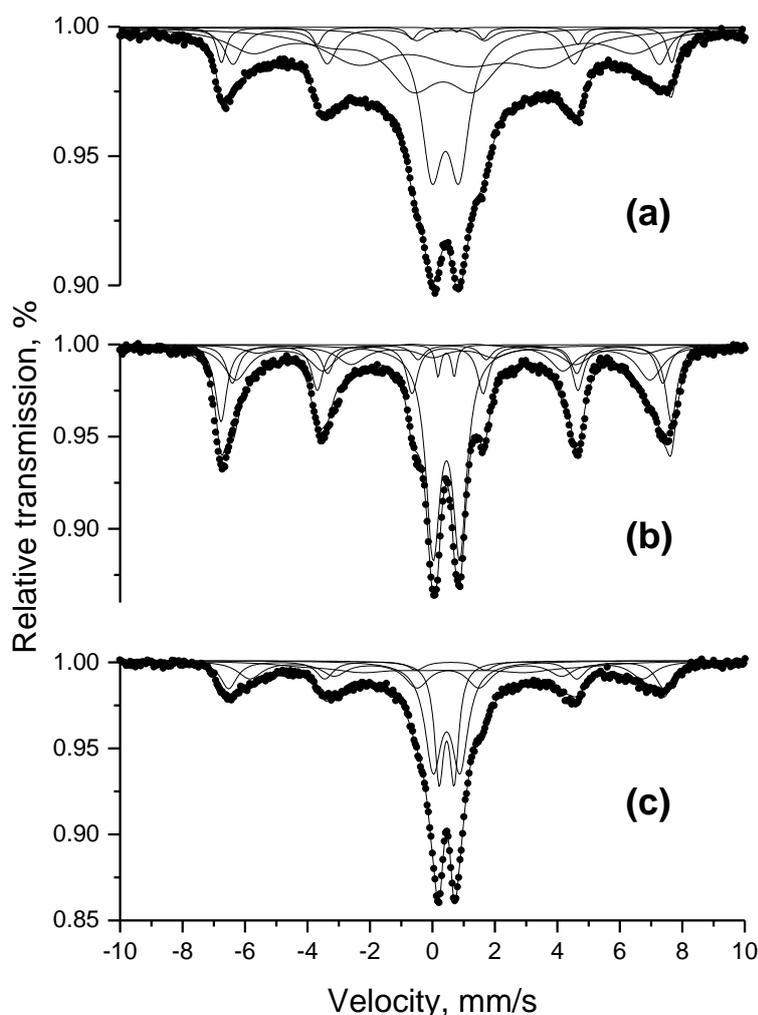


Figure 2. LNT Moessbauer spectra of co-precipitated $Ni_{0.5}Fe_{2.5}O_4$ material (a), the same material after thermal treatment (b) and after mechanochemical treatment (c).

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List of used abbreviations:

liquid nitrogen temperature (LNT);
 room temperature (RT);
 X-ray diffraction (XRD);

5 References

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