Mechanochemically prepared mono- (Cu, Ni), bi- (Cu/Sn, Ni/Sn) and trimetallic (Cu/Ni/Sn) nanoparticles – structural characterization and some catalytic applications

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PhD Theses

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1. Introduction and aims

The properties of the atoms residing on the surface of a nanoparticles are much closer to those of the free atoms than to those of the bulk. The effects of nano-size are manifested in a variety of ways including the optical, electrical, mechanical, chemical, physico-chemical and magnetic properties, among others.

In principle, there are two well-known, fundamentally different ways to prepare a nanoparticle: the *top-down* and the *bottom-up* methods. The first so-called *top-down* method includes the transformation of the larger size bulk starting material to nano-sized objects *via* mechanical, chemical or physical means, while the *bottom-up* approach commences from the atomic level.

Mechanochemistry is usually classified as a *top-down* technique, but there are *bottom-up* ways of using it as well. Mechanochemistry embraces all the processes, which are initiated *via* mechanical energy input resulting in the desired chemical and/or physico-chemical transformations. This may take place through transforming a given precursor with mechanical energy into a new compound or *via* changing the structure of the starting material with mechanical activation. Shearing, pressing and grinding are typical mechanochemical approaches. Mills of various types are the most commonly used pieces of mechanochemical equipment. Large variety of them are employed in the industrial practice, therefore mechanochemical syntheses fine-tuned in the laboratory can be scaled up to industrial scale mass production more readily than other synthesis methods. Clearly, this is one of the main advantages of performing syntheses by using mechanochemistry.

Metallic nanoparticles are routinely used in a large variety of heterogeneous catalytic applications. These are remarkably environmentally friendly, since the catalyst and the reaction mixture reside in different phases. Therefore, the catalyst can readily be separated from the reaction mixture and can be reused. There are, however, a large number of other potential applications associated with metallic nanoparticles including the future substitution of fossil energy sources, handling of global warming and controlling green-house gases. Clearly, the academic world as well as the environmentally aware part of the public has great expectations regarding the progress of the ongoing research of metallic nanoparticles.

During my PhD thesis work, the main task was the mechanochemical preparation of mono- (Cu, Ni), bi- (Cu/Sn and Ni/Sn) trimetallic (Cu/Ni/Sn) nanoparticles using a ball mill. The aim of the research was to establish, how the instrumental parameters (milling frequency, milling time, effect of the quality and quantity of additives, *etc*.) used during the

syntheses of the nanoparticles affect the quality (structure, morphology, size) of the products. This way we attempted to optimize the experimental conditions on one end, and to work out the control of the parameters to synthesize nanoparticles with predictable size, composition and structure on the other.

Therefore, we embarked on an experimental program, during which the instrumental parameters were systematically varied, and their effect on the structure of the nanoparticles obtained was scrutinized. We also attempted to establish the effect of the quality and quantity of various additives on the products obtained, *via* using a set ensemble of previously optimized instrumental parameters. The effects of synthesis parameters on the aggregation of the nanoparticles were examined. The catalytic performance of selected monometallic nanoparticle preparations were applied in Ullmann-type and Suzuki-Miyaura coupling reactions.

2. Experimental part

The nanoparticles were primarily prepared *via* using the mechanochemical route, with a RETSCH MM 400 ball mill. During the initial phases, the grinding parameters were optimized. Following this, the grinding parameters were kept constant and a number of additives were employed to aid the syntheses of the mono-, bi-, and trimetallic nanoparticles.

In all cases, the products were analyzed by using powder X-ray diffractometry (XRD). On the basis of the XRD patterns and with the help the JCPDS database, the components of the products were identified. This assisted us in establishing, whether the metals were present in the elemental state or (for bi- and trimetallic systems) some sort of alloy was formed during the synthesis. Primary particle diameters were obtained from the Scherrer equation. Scanning electron microscopy (SEM) was employed to establish the changes of the surface and the morphology of the particles taken place during the mechanical treatment. The energy dispersive X-ray analysis (EDX) coupled with the SEM provided a very useful semi-quantitative information on the distribution of various components in the products. Transmission electron microscopy (TEM) was used for the observation of the primary particles as well as the aggregates formed. From the perspective of possible applications in heterogeneous catalysis, the knowledge of the degree of dispersion of the catalysts is essential, and the SEM and TEM images attested that the nanoparticles were aggregated to a certain extent. To obtain a more refined view, dynamic light scattering measurements (DLS) were carried out, which resulted in the hydrodynamic radius and the

degree of polydispersity (characterized by the PDI, polydispersity index). During the catalytic tests, the results from the DLS measurements were employed in the sense, *i.e.* the most dispersed, that is, the catalyst with the largest specific surface area was selected for these experiments. As supplementary methods, FT-IR spectroscopic measurements and specific surface area determinations *via* the BET method were performed.

3. Novel scientific results

1. We were the first to use dimethyl sulfoxide (DMSO) as additive during the mechanochemical preparation of Cu nanoparticles, and to prove that DMSO was an excellent stabilizing agent being suitable to inhibit aggregation of copper nanoparticles *via* cold welding or van der Waals interactions.

We have shown that upon DMSO addition, the primary particle size of the nanoparticles thus obtained passes through a maximum with the increasing amount of DMSO. From the XRD of the samples, the formation of some Cu_2O was observed on the specimen which had the largest primary particle size. From DLS measurements, the degree of aggregation was found to be the smallest for the Cu nanoparticles prepared in presence of DMSO.

2. During the milling, beside the Cu nanoparticles, Cu(I) ions were also formed, and the thus obtained Cu/Cu_2O nanocomposite proved to be efficient catalyst in the Ullmann-type coupling reaction of iodobenzene and 1H-pyrazole.

The untreated Cu powder displayed poor catalytic activity, which was significantly improved even by using dry milling. Further significant improvement was observed when the milling was carried out in the presence of various additives, in particular, in the presence of DMSO. This effect was explained in terms of the presence of Cu_2O (*ca.* 1%w/w) on the surface of the Cu nanoparticles. This verifies, the received knowledge that the efficiency of the Cu catalysts in the Ullmann reaction can be significantly enhanced if Cu(I) ions.

3. The preparation of nanoparticles *via* $Ni(OH)_2$ reduction with hydrazine was combined with mechanical pretreatment for the first time, and was shown that this pretreatment resulted in significant improvement in the catalytic activity of the nanomaterials.

The mechanochemical pretreatment of the $Ni(OH)_2$ precursor was found to exert profound improvement on the catalytic activity of the Ni nanoparticles obtained from them relative to the untreated precursor. From DLS and SEM measurements, the pretreatment has no significant effect on the size of the aggregates formed from the primary particles and the specific surface areas of the specimens are also constant. Therefore, it can be hypothesized, that improved catalytic activity is associated with the increase in the number of surface defects which are retained during reduction.

4. Cu/Sn bimetallic nanoparticles were successfully prepared *via* the mechanochemical route by adding various solid and liquid additives to the reaction mixture. Interrelations were established between the quality of the additive and the structure and composition of the products.

Eight different additives were employed during the synthesis of Cu/Sn bimetallic nanoparticles. From XRD and SEM-EDX measurements, it has been established that the quality of the product (alloy or physical mixture) depended on the quality of the additive. Upon adding NaCl or heptane, the quantitative formation of Cu_6Sn_5 (η-bronze) was observed, and the degree of transformation was found to be independent of the amount of additive. Addition of oleil-amine (OAm), ethylene glycol (EG) and polyethylene glycol (PEG) resulted in the formation of the physical mixture of Cu and Sn. Polyvinil pyrrolidinon (PVP), cetyl trimethyl ammoniumbromide (CTAB) and Na-dodecyl sulfate (SDS) yielded η-bronze at the smallest additive concentrations. With increasing additive amounts, the amount of the alloy gradually decreased and the fraction of physical mixture increased.

5. It has been demonstrated that the size of the nanoparticle aggregates can be fine-tuned and varied over a wide range if the amount of additive present is carefully chosen.

From DLS measurements, it has been shown that an increase in the amount of the additives, solid at room temperature (NaCl, PVP, CTAB, SDS), predominantly results in an increase in the size of the aggregates. Liquid additives (OAm, EG, PEG, heptane) cause an opposite relation. Therefore, the aggregation is primarily determined (at least significantly influenced) by the consistence of the additive.

6. Comparing the additive dependence of the composition and the structure of mechanochemically prepared Ni/Sn bimetallic nanoparticles with the Cu/Sn ones, similarities prevail and some striking differences are also observed.

In the effect of various additives on the structure of Ni/Sn bimetallic nanoparticles, three kinds of products were observed similarly to those observed for the Cu/Sn system. The effect of OAm is identical for the two systems, here, the physical mixture of Ni and Sn is obtained, too. PVP, CTAB, SDS and EG resulted in the formation of physical mixture and some alloys, just like in the Cu/Sn case. However, the alloy thus formed is not one particular alloy but a mixture of two or three, with the general formula of Ni_xSn_y. In the presence of NaCl and heptane, the alloy formation is preferred, but here too the mixture of various alloys in various proportions was observed.

7. The patterns of product compositions established for the two bimetallic systems are followed in the trimetallic systems too; the only remarkable difference is that under the conditions employed, the preferred formation of the η-bronze was observed and the presence of Ni_xSn_y alloys was not possible to be detected.

Upon milling, in the presence of PEG and OAm, in the trimetallic Cu/Ni/Sn systems, the constituent metals are present separately in the product. Adding SDS, EG, PVP or CTAB to the reaction mixture, the partial formation of η-bronze was observed, the amount of it increased in the order of SDS > EG > PVP > CTAB. The constituents which were not alloyed, are present as separate phases in the product, and the Ni_xSn_y alloy does not seem to form. In the presence of NaCl and heptane, the Cu and Sn content of the mixture quantitatively formed the Cu_6Sn_5, and Ni was found to be present as a separate phase. Accordingly, under the experimental conditions used, the presence of NaCl and n-heptane results in the preferred formation of the η-bronze over Ni_xSn_y alloy.

4. Application and "green" aspects of the results

The catalytic application of the metal nanoparticles is well-known. During my PhD studies, our primary goal was the synthesis of mono-, bi-, and trimetallic nanoparticles with the perspective of their heterogeneous catalytic application. Heterogeneous catalysis is an environmentally benign technique, as opposed to homogeneous catalysis. Using the latter, the removal of the catalyst from the reaction mixture is often problematic, and the solvent in large excess relative to the catalyst enters in the environment. In heterogeneous catalysis, the

removal of the catalyst is usually easy, leaching is in general insignificant, and the catalyst can be reused. Nanoparticles can be immobilized on solid supports, therefore they represent a particularly attractive way of catalyst preparation.

The synthesis of nanostructured materials, however, is often scrupulous from environmental protection point of view depending on the type of synthesis used. In some cases, the solvent need is enormous, the formation of unwanted side products or toxic wastes may also be problematic. The great advantage of the mechanochemical nanoparticle preparation is the simplicity, the low cost, and, even more importantly, the lack of solvent during the synthesis and excellent atom efficiency. For this reason, the synthesis technique used by us, mechanochemistry that is, has several advantages in the preparation of metallic nanoparticles in both the laboratory and the industrial scale.

5. Publications and conference participations

5.1 Full papers directly related to the theses published in peer-reviewed journals

1. **K. Musza**, M. Szabados, A. A. Ádám, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Mechanochemically modified hydrazine reduction method for the synthesis of nickel nanoparticles and their catalytic activities in the Suzuki-Miyaura cross-coupling reaction
Reaction Kinetics Mechanisms and Catalysis, 2019, 126, pp. 857-868.
IF_{2018}: 1,428

2. **K. Musza**, M. Szabados, A. A. Ádám, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Ball milling of copper powder under dry and surfactant-assisted conditions – on the way towards Cu/Cu_2O nanocatalyst
Journal of Nanoscience and Nanotechnology, 2019, 19, pp. 389-394.
IF_{2018}: 1,354

5.2 Full papers directly related to the theses published in conference proceedings

1.**K. Musza**, M. Szabados, A. A. Ádám, P. Sipos, I. Pálinkó: Preparation of Cu-Sn bimetallic nanoparticles via ball milling – the effect of various additives on the structure
XXVII. International Conference on Coordination and Bioinorganic Chemistry, Vol.14, Modern Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, 2019, ISBN 978-80-8208-014-1, pp. 50-57.

2. Sz. Lantos, **K. Musza**, M. Szabados, A. A. Ádám, T. Pásztor, P. Sipos, I. Pálinkó: $Ni(OH)_2$ hidrazinos redukciójával előállított Ni nanorészecskék jellemzése és katalitikus aktivitása (Characterization and catalytic activities of Ni nanoparticles prepared via reduction of $Ni(OH)_2$ with hydrazine)
XLI. Kémiai Előadói Napok, Előadás összefoglalók, 2018, ISBN 978-963-9970-95-3, pp. 87-90.

3. **K. Musza**, A. A. Ádám, M. Szabados, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: The effect of the experimental parameters on the formation of Cu/Cu_2O nanoparticles
XXVI. International Conference on Coordination and Bioinorganic Chemistry, Vol.13, Modern Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, 2017, ISBN 978-80-89597-65-9, pp. 93-97.

5.3 Full papers not directly related to the theses published in peer-reviewed journals

1. A.A. Ádám, M. Szabados, G. Varga, Á. Papp, **K. Musza**, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Ultrasound-assisted hydrazine reduction method for the preparation of nickel nanoparticles, physicochemical characterization and catalytic application in Suzuki-Miyaura cross-coupling reaction
Nanomaterials, 2020,10, pp. 632:1-18.
IF_{2018}: 4,034

2. A. A. Ádám, M. Szabados, **K. Musza**, P. Bélteky, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Effect of medium and nickel salt source in the synthesis and catalytic performance of nano-sized nickel in the Suzuki-Miyaura cross-coupling reaction
Reaction Kinetics Mechanisms and Catalysis, 2019, 126, pp. 841-855.
IF_{2018}: 1,428

3. A. A. Ádám, M. Szabados, Á. Polyákovics, **K. Musza**, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: The synthesis and use of nano nickel catalysts
Journal of Nanoscience and Nanotechnology, 2019, 19, pp. 453-458.
IF_{2018}: 1,354

5.4 Other full papers not directly related to the theses published in conference proceedings

1. Á. Polyákovics, A. A. Ádám, M. Szabados, **K. Musza**, G. Peintler, P. Sipos, I. Pálinkó: Méretkontrollált Ni nanorészecskék előállítása és jellemzése
XL. Kémiai Előadói Napok, Előadás összefoglalók, 2017, ISBN 978-963-9970-83-0, pp. 243-247.

2. A.A. Ádám, **K. Musza**, M. Szabados, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Synthesis and characterization of nickel nanoparticles
XXVI. International Conference on Coordination and Bioinorganic Chemistry, Vol.13, Modern Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, 2017, ISBN 978-80-89597-65-9, pp. 7-13.

5.5 Presentations and posters related to the present theses

1. **K. Musza**, M. Szabados, A.A. Ádám, P. Sipos, I. Pálinkó: Preparation of Cu-Sn bimetallic nanoparticles *via* ball milling – the effect of various additives on the structure
XXVII. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovak Republic (oral presentation), 2019.

2. Sz. Lantos, **K. Musza**, M. Szabados, A.A. Ádám, T. Pásztor, P. Sipos, I. Pálinkó: $Ni(OH)_2$ hidrazinos redukciójával előállított Ni nanorészecskék jellemzése és katalitikus aktivitása (Characterization and catalytic activities of Ni nanoparticles prepared via reduction of $Ni(OH)_2$ with hydrazine)
XLI. Kémiai Előadói Napok, Szeged, Magyarország (oral presentation), 2018.

3. **K. Musza**, M. Szabados, A.A. Ádám, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Mechanochemically modified hydrazine reduction method for the synthesis of nickel nanoparticles and their catalytic activity
1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, Budapest, Magyarország (oral presentation), 2018.

4. **K. Musza**, M. Szabados, A.A. Ádám, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Preparation, characterization and catalytic activity of Cu-Sn bimetallic nanopowder synthesised *via* mechanical milling
1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, Budapest, Magyarország (poster), 2018.

5. **K. Musza**, M. Szabados, A.A. Ádám, P. Sipos, I. Pálinkó: The effect of the experimental parameters on the formation of Cu/Cu_2O nanoparticles
XXVI. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovak Republic (presentation), 2017.

5.6 Other presentations and posters not directly related to the theses

1. A.A. Ádám, Á. Papp, M. Szabados, **K. Musza**, P. Sipos, I. Pálinkó: Synthesis and characterization of LDH-supported Ni, Cu or NiCu nanoparticles
XXVII. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovak Republic (oral presentation), 2019.

2. A.A. Ádám, Á. Papp, M. Szabados, **K. Musza**, P. Sipos, I. Pálinkó: $Al(OH)_3$ hordozóra felvitt Ni, Cu és NiCu nanorészecskék előállítása és jellemzése
I. FKF Szimpózium, Debrecen, Hungary (oral presentation), 2019.

3. A.A. Ádám, M. Szabados, **K. Musza**, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Synthesis of nickel nanocatalysts by ultrasound irradiation under different conditions
14th Pannonian International Symposium on Catalysis, Starý Smokovec, Slovak Republic (oral presentation), 2018.

4. A.A. Ádám, M. Szabados, **K. Musza**, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Effect of medium and nickel salt source in the synthesis of nano-sized nickel catalysts
1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, Budapest, Hungary (oral presentation), 2018.

5. A.A. Ádám, M. Szabados, **K. Musza**, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Application of ultrasound irradiation in the syntheses of nickel nanocatalysts
1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, Budapest, Hungary (poster), 2018.

6. A.A. Ádám, **K. Musza**, M. Szabados, Á. Papp, P. Sipos, I. Pálinkó: Hydrazine reduction method for preparing copper-nickel bimetallic nanoparticles
2nd Young Researchers' International Conference on Chemistry and Chemical Engineering, Budapest, Hungary (oral presentation), 2018.

7. Á. Polyákovics, A.A. Ádám, M. Szabados, **K. Musza**, G. Peintler, P. Sipos, I. Pálinkó: Méretkontrollált Ni nanorészecskék előállítása és jellemzése
XL. Kémiai Előadói Napok, Szeged, Hungary (oral presentation), 2017.

8. M. Szabados, **K. Musza**, T. Pásztor, P. Sipos, I. Pálinkó: Nikkel nanorészecskék előállítása különféle alkoholokat tartalmazó közegben
Vegyészkonferencia, Hajdúszoboszló, Hungary (poster), 2017.

9. A.A. Ádám, **K. Musza**, M. Szabados, P. Sipos, I. Pálinkó: Synthesis and characterization of nickel nanoparticles
XXVI. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovak Republic (oral presentation), 2017.

Peer-reviewed papers total: 5,	out of this, related to the topic of thesis: 2
Cumulative impact factor: 9,598	out of this, related to the topic of thesis: 2,782