

PhD Theses

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION  
OF NICKEL-CONTAINING NANOCATALYSTS

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## **1. Introduction and aims**

Nowadays, the synthesis, characterization of nanosystems and their integration into larger systems become more and more popular. Thanks to their special properties they are used in many applications, such as electronics, pharmaceuticals, as heterogeneous catalysts *etc.* A significant proportion of the industrial syntheses is carried out catalytically, due to the fact that the catalytic reactions have higher atomic efficiency and thus exert less burden on the environment than the stoichiometric reactions. In the literature, several examples can be found for application of Pd and Pt as nanocatalysts in cross-coupling reactions. In recent years, these catalysts were replaced with economically more viable metal and metal oxides like nickel, the element that we also used in the syntheses of our catalysts. These catalysts are not only cheaper, but they are also greener than the previously used counterparts.

Aims of our work were to synthesize Ni nanoparticles, and apply them as catalyst in a ligand-free Suzuki-Miyaura cross-coupling reaction. The catalysts were synthesized with chemical reduction, because this is a simple and cost-effective method. During the syntheses we gained comprehensive picture about the effects of the nickel-salt precursor, the temperature and the stirring. In addition to mechanical stirring we also studied the effect of ultrasound irradiation at varying power and intensity on the system with the help of a sonotrode. The catalytic properties of Ni nanocatalysts were studied in a model reaction (preparation of biphenyl from iodobenzene and phenylboronic acid). Furthermore, we investigated the structural changes of the used catalysts.

Our research group previously has collected much experience on the synthesis and catalytic applications of layered double hydroxides (LDH). Since the catalytic properties of nanoparticles can be enhanced with the application of supports, it seemed worthwhile to use the accumulated knowledge for the preparation of supported Ni catalysts.

The results obtained will be described in chapter 3 under the title "Novel scientific results".

## **2. Experimental part**

### **2.1. Synthesis of nickel nanoparticles**

Ni nanoparticles were synthesized with chemical reduction from various nickel salts, at different temperatures. The properties of the products obtained from the mechanically stirred, non-stirred and ultrasound-assisted syntheses were compared. During the syntheses, the nickel

salt solution (0.1 M) and the ethanolic solution of hydrazine and KOH were mixed at set temperatures (5, 25, 50 and 75°C) for 4 h. The nanoparticles thus obtained were filtered, washed with ethanol and distilled water, and dried under inert atmosphere.

The catalytic properties of the nanoparticles were studied in a ligand-free Suzuki-Miyaura cross-coupling reaction. During the reuse of nanoparticles, the structure of Ni nanocatalysts changed, thus, the results of these transformations and their effects on their catalytic properties were also studied. The structural changes were investigated *via* using different solvents (*N,N*-dimethylformamide, dimethylsulphoxide, ethanol or toluene) at reflux temperature. The catalytic properties of Ni nanoparticles with different structures were studied in the catalytic oxidation of toluene.

Since the catalytic properties of nanoparticles can be enhanced with supports, nanocatalyst systems containing Ni of different oxidation states were also synthesised. The Ni(II)-containing, aluminium-rich layered double and triple hydroxides were obtained by the gibbsite intercalation technique. In the first step, the Al(OH)<sub>3</sub> was activated by ball milling (6 h, 12 Hz), and then a nickel-salt and distilled water were added to the activated hydroxide. The mixture was agitated at 85°C for 3 days. The precipitates were filtered, washed and dried. The Ni nanoparticles were deposited onto the surface of the aluminium-rich NiAl-LDH at 1, 3, 5, 10 and 15 w/w% concentration, and their catalytic properties were investigated in the CO<sub>2</sub> hydrogenation reaction.

## 2.2. Experimental techniques

Powder X-ray diffractograms (XRD) in the  $\theta = 4 - 80^\circ$  range were recorded on a Rigaku Miniflex II instrument with 4°/min scan speed using CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The reflections appearing in the normalized diffractograms were assigned with the help of the JCPDS-ICDD (Joint Committee of Powder Diffraction Standards- International Centre for Diffraction Data) database. The primary particle sizes of the nanoparticles were estimated from the most intense (111) reflections using the Scherrer equation with using a shape factor of 0.9.

A Malvern NanoZS dynamic light scattering (DLS) instrument operating with a 4 mW helium-neon laser light source ( $\lambda = 633 \text{ nm}$ ) was used to map the heterogeneity in the solvodynamic diameters of the aggregated nanoparticles at room temperature. The measurements were performed in back-scattering mode at 173°, and the nanoparticles were pre-dispersed in ethylene glycol for 1 h by ultrasonic irradiation. The concentration of the light-gray semi-transparent dispersion was 0.1 g/dm<sup>3</sup>.

The morphology and size of the nanocrystals were examined by scanning electron microscopy (SEM-Hitachi S-4700 instrument) and transmission electron microscopy (TEM-FEI TECHNICAL G220 X-TWIN instrument). The elemental analysis was performed by energy dispersive X-ray (EDX) investigations (Röntec QX2 spectrometer equipped with Be window and coupled to the SEM).

In order to gain information about the thermal behaviour of nanoparticles between 25 and 1000°C, the dried samples were analysed by a Setaram Labsys derivatograph applying constant flow of air at 3°C/min heating rate. For the measurements, 15–25 mg of the samples were placed into high-purity alpha alumina crucibles.

The basic and acid sites of the samples were characterized by temperature programmed desorption (TPD) using 99.9% CO<sub>2</sub>/He and 99.3% NH<sub>3</sub>/He respectively. TPDs were performed on a Hewlett-Packard 5890 gas chromatograph equipped with thermal conductivity detector. Before the measurements, the samples were purified by heat treatment at 300°C for 3 h.

The N<sub>2</sub> adsorption-desorption isotherms were registered on a Quantachrome NOVA 3000e instrument. The nanoparticles were degassed at 200°C for 3 h in vacuum to remove the adsorbed impurities. The specific surface areas were calculated by the Brunauer-Emmett-Teller equation from the adsorption branches, and the determination of the average pore sizes and total pore volumes were estimated from the desorption branches by the Barrett-Joyner-Halenda equation.

The Fourier-transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-4700 spectrophotometer with 4 cm<sup>-1</sup> resolution accumulating 256 scans. The spectrometer was equipped with a DTGS detector and a ZnSe ATR accessory. The structural features of the solids were analysed in the 4000–500 cm<sup>-1</sup> wavenumber range.

### 3. Novel scientific results

**T1. The chemical quality of the starting nickel salt and the reaction temperature together influence the outcome of the synthesis, the composition of the product, the size of the nanoparticles, the tendency of the aggregation and the catalytic properties.**

The X-ray diffractograms reveal that phase-pure nickel nanoparticles could be synthesized at higher temperature (75°C) regardless of precursor quality. At lower temperatures (50 and 25°C) the success of the reactions varied. The degree of conversion was clearly influenced by the stability of the complexes formed from the ions of the starting nickel salt, and the starting materials with lower complex stability constants were highly reactive even under mild conditions. The dynamic light scattering results suggest that the size and dispersity of aggregates were different. Furthermore, the transmission electron microscopy images showed that the aggregates were always composed of smaller spheres (primary particles), thus, they are polycrystallites.

**T2. We were the first to use ultrasound treatment with variable parameters in the hydrazine reduction synthesis of nickel nanoparticles. The ultrasound irradiation was found to exert significant effect on crystal nucleation and crystal growth and thus on the structural, surface, the thermal and the catalytic properties of the nanoparticles.**

Using NiI<sub>2</sub> as the starting material, the findings obtained from X-ray diffractometry and infrared spectroscopy suggested that the nickel-hydrazine-iodide complex underwent structural and composition changes due to the special conditions induced by ultrasound irradiation (high temperature and pressure, high kinetic energy). These affected the formation of Ni(OH)<sub>2</sub> intermediate, thus influencing the formation and properties of the nickel nanoparticles.

**T3. The face centred cubic (fcc) nickel nanoparticles could be partially transformed to hexagonal close packed (hcp) ones by solvothermal method at high temperature, without using surfactant.**

It was found that the nanoparticles kept in dimethylsulphoxide at reflux temperature for 24 h transformed to nickel sulphide in full. In *N,N*-dimethyl-formamide the fcc nanoparticles partially transformed to hcp with nickel oxide impurities. Carrying out the same reaction in ethanol, half of the fcc transformed to hcp.

**T4. We were the first to synthesize the phase-pure aluminium-rich CuAl-layered double hydroxide by mechanochemical gibbsite intercalation technique.**

By preparing the phase-pure NiCuAl-, NiCoAl-, NiZnAl-, CuCoAl- and CuZnAl-layered triple hydroxides, we were able to supplement the known metal ion incorporation affinity series with Cu<sup>2+</sup> ion: Ni<sup>2+</sup>>Cu<sup>2+</sup>>Co<sup>2+</sup>~Zn<sup>2+</sup>. The results of energy dispersive X-ray analysis suggested that

the Cu<sup>2+</sup> ions were incorporated into the aluminium-rich layered triple hydroxides in a quarter of the molar amount compared to Ni<sup>2+</sup> ions and in ninefold molar amounts as Co<sup>2+</sup> and Zn<sup>2+</sup> ions.

**T5. Aluminium-rich Ni-containing layered double hydroxide were used for the first time as supports for Ni nanoparticles in CO<sub>2</sub> hydrogenation reaction.**

Ni nanoparticles were deposited onto the surface of the aluminium-rich NiAl-LDH in 1, 3, 5, 10 and 15 w/w% concentrations. The catalytic properties of these composites were studied in CO<sub>2</sub> hydrogenation reaction.

## 4. Application of the results

The results presented here are of basic research character; nevertheless, the frequently used Pd and Pt catalysts have been changed to Ni nanocatalysts in the Suzuki-Miyaura cross-coupling reaction. This way economic viability and green chemistry approach were displayed, which are important factors in industry. Furthermore, during the CO<sub>2</sub> hydrogenation reaction, the synthesized Ni/NiAl-LDH-composites proved to be promising catalyst.

## 5. Publications

### 5.1. Papers related to the Theses published in refereed journals

[1] **Ádám A.A.**, Szabados M., Polyákovics Á., Musza K., Kónya Z., Kukovecz Á., Sipos P., Pálinkó I.:

The synthesis and use of nano nickel catalysts,

*Journal of Nanoscience and Nanotechnology* **19**, 453–458 (2019)

Impact factor: 1,093<sub>2018</sub>

[2] **Ádám A.A.**, Szabados M., Musza K., Béltéky P., Kónya Z., Kukovecz Á., Sipos P., Pálinkó I.:

Effect of medium and nickel salt source in the synthesis and catalytic performance of nanosized nickel in the Suzuki-Miyaura cross-coupling reaction,

*Reaction Kinetics Mechanisms and Catalysis* **126**, 841–855 (2019)

Impact factor: 1,428<sub>2018</sub>

[3] **Ádám A.A.**, Szabados M., Varga G., Papp Á., Musza K., Kónya Z., Kukovecz Á., Sipos P., Pálinkó I.:

Ultrasound-assisted hydrazine reduction method for the preparation of nickel nanoparticles, physicochemical characterization and catalytic application in Suzuki-Miyaura cross-coupling reaction,

*Nanomaterials* **10**, 632:1–18 (2020)

Impact factor: 4,034<sub>2018</sub>

## 5.2. Papers related to the Theses published as full papers in conference proceedings

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

[2] **Ádám A.A.**, Musza K., Szabados M., Sipos P., Pálinkó I.:  
Synthesis and characterization of nickel nanoparticles,  
*Modern Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry*, Szlovákia,  
Slovak Chemical Society, 2017, pp. 7–13.

[3] Papp Á., **Ádám A.A.**, Szabados M., Sipos P., Pálinkó I.:  
Alumíniumban gazdag réteges kettős és hármas hidroxidok előállítása, szerkezetük jellemzése,  
*XLII. Kémiai Előadói Napok Előadásösszefoglalók*, ISBN: 978-615-6018-01-4, Szeged, 2019,  
pp. 111–116.

## 5.3. Other papers published in refereed journals

[1] Sipiczki M., **Ádám A.A.**, Anitics T., Csendes Z., Peintler G., Kukovecz Á., Kónya Z., Sipos P., Pálinkó I.:  
The catalytic epoxidation of 2-cyclohexene-1-one over uncalcined layered double hydroxides  
using various solvents,  
*Catalysis Today* **241**, 231–236 (2015)  
Impact factor: 4,02

[2] Truong N.H., **Ádám A.A.**, Varga G., Dudás Cs., Kele Z., Sipos P., Pálinkó I.:  
Thionation of cyanoxime derivative to form the sulphur-containing derivative, a novel ligand  
for complexation with transitional metal ions,  
*Structural Chemistry* **28**, 475–478 (2017)  
Impact factor: 1,957

[3] Szabados M., **Ádám A.A.**, Kónya Z., Kukovecz Á., Sipos P., Pálinkó I.:  
Effect of ultrasonic irradiation on the synthesis, crystallization, thermal and dissolution  
behaviour of chloride-intercalated, co-precipitated CaFe-layered double hydroxide,  
*Ultrasonics Sonochemistry* **55**, 165–173 (2019)  
Impact factor: 7,279<sub>2018</sub>

[4] Musza K., Szabados M., **Ádám A.A.**, Kónya Z., Kukovecz Á., Sipos P., Pálinkó I.:  
Ball milling of copper powder under dry and surfactant-assisted conditions – on the way  
towards Cu/Cu<sub>2</sub>O nanocatalyst,  
*Journal of Nanoscience and Nanotechnology* **19**, 389–394 (2019)

