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ORGANOMETALLIC CATALYSTS IMMOBILIZED ON MAGNETIC NANOPARTICLES

(KATALIZATORY METALOORGANICZNE IMMOBILIZOWANE NA NANOCZĄSTKACH MAGNETYCZNYCH)

ABSTRACT

Doctoral thesis develop a wide topic of heterogenic, organometallic catalysts, which were anchored on magnetic solid support (magnetic nanoparticles). In the theoretical part one can find a review about usage of magnetic nanoparticles as solid support for catalysis. Also commonly used ligands and capping agents applied for stabilization of nanoparticles were catalogued. Catalytic properties, stability and recycling of heterogeneous catalysts were compared and discussed.

The research part was divided into two parts which represent two strategies of anchoring catalysts on the magnetic surface. Nanoparticles which were used for the preparation of the catalysts were iron oxides. First strategy was direct synthesis of ligands (especially NHC ligands) on the surface of magnetic nanoparticles (MNP). Second strategy is RAFT/MADIX polymerization which is initiated direct from the surface of MNP. In both strategies final catalyst (organometallic complex with palladium or copper) was synthesized directly on the solid phase (as an ultimate step of catalyst preparation) – this is the most commonly used approach for preparation of magnetically separable heterogeneous catalysts. The first step of the catalysts preparation was stabilization of MNP by siloxane coating, made from 3-aminopropyltrimethoxysilane. This layer not only stabilized nanoparticles but also introduced terminal amino groups which were further modified to form NHC precursor or CTA agent – dithiocarbonate (for RAFT/MADIX polymerization).

Herein, comparison of activity of palladium catalysts which were made by different methods was attempted. Additionally, the influence of the ligands structure (first strategy) and the influence of the polymeric shell structure (second strategy) on the heterogeneous catalysts activity was studied

First strategy was used for preparation of three different NHC ligands anchored on the surface of magnetic nanoparticles. These ligands were further used for preparation of: one palladium complex and four copper complexes. Palladium catalysts had great activity in the Heck cross coupling reaction when iodo- and bromoarenes were used. After reuse this catalyst was active up to five times.

Furthermore, four different copper catalysts were made. Their differed in oxidation state of copper and in the structure of NHC ligand. Their activity in CuAAC “click” reactions was tested. Surprisingly, complexes which had copper(II) in their structure showed better catalytic activity than copper(I) catalysts. Usage of copper(II)-NHC complexes anchored on magnetic nanoparticles as catalysts in CuAAC reactions lower the costs of the synthesis, Cu(II) salts are cheaper and easier to handle. Furthermore, providing the reactions catalyzed by them did not require addition of a base or even reducing agent

(sodium ascorbate) which is obligatory when common Cu(II) complexes are used (for reducing Cu(II) to active Cu(I) species).

In the second strategy the polymeric layer, with complexing activity, onto magnetic surface was prepared. Three bifunctional monomers were synthesized: two acetylacetonate derivatives and one unsaturated NHC precursor (imidazolium salt). Subsequently, two of them were used for the creation of several polymeric shells onto magnetic surface, which differed in chemical structure and architecture. Several polymeric shells were created: homopolymeric, block copolymeric and random copolymeric. In this strategy, magnetic-polymer hybrids were obtained and used for preparation of palladium catalysts which were active in Heck cross coupling reactions. The best results were obtained when nanoparticles with homopolymeric shells were used as complexing agents. The catalysts were used in the amount of 1mol%, and the highest obtained yield was 64% in the reaction of *n*-butyl acrylate and iodobenzene.

In the experimental part all of synthetic procedures were described and full spectroscopic characterization of obtained products was presented.

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