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EPOXY SUPPORTS FOR METAL COMPLEX CATALYSTS SYNTHESIS, FEATURES AND APPLICATIONS

ABSTRACT

Presented thesis is devoted to research on the synthesis, characterization and use of highly selective catalytic systems composed of transition metal complexes heterogenised on functionalized epoxy resins by thiourethane oligomers. This work presents results of research on synthesis and catalytic activity of new metal complex catalysts immobilized under the standard and supercritical carbon dioxide conditions ($scCO_2$).

A novel thiol-terminated thiourethane oligomers were synthesized from low-molecular weight di- and multifunctional mercaptans and diisocyanates and employed as curing agent for epoxy resin. The results of this study indicate that molecular structure and functionality of thiourethane oligomers are of critical importance in governing the curing mechanism, structure of the network and final properties of epoxy compositions.

The application of epoxy resin cured with polythiourethane hardeners as novel and efficient support for palladium and platinum complex catalyst was examined in my thesis. The effects of this study indicate that thiourethane oligomers used to cure epoxy resin can greatly affect the catalytic properties of the resin-supported palladium and platinum catalyst. These new type of polymer supports comparing to other organic carriers offers several practical advantages such as ability to control the crosslinking density, porosity and the chemical structure of the polymeric matrix, which influence the catalytic properties of the immobilized metal complex.

Additionally, the use of supercritical CO_2 enabled a better distribution of the metal complex on the surface of polymer matrix. The presence of the functional groups allows to obtain catalysts, wherein the metal centers have a different electronic structure and various degrees of oxidation, thus such systems are characterized by high selectivity. The development

and optimization of a reproducible method of obtaining complex catalysts on polymer matrices under supercritical CO_2 was one of the main objective of the research.

The characteristic of polymeric supports and heterogenized palladium and platinum catalysts involve research methods like: time-of-flight secondary ion mass spectrometry (ToF-SIMS), ^{1}H NMR spectroscopy, infrared spectroscopy (IR), scanning electron microscopy (SEM-EDX), nitrogen sorption measurement (BET), differential scanning calorimetry (DSC), X-ray electron spectroscopy (XPS), atomic absorption spectroscopy (AAS). Activity of the prepared catalysts was examined in the Heck reaction and the hydrogenation of cinnamaldehyde under pressure.

The development of new complex catalysts expands knowledge in the field of chemical catalysis. The palladium and platinum catalysts immobilized on epoxy supports have a high activity and stability during reuse. The innovative of the proposed solution lies in the ability to modeling the catalytic properties for the specific chemical processes. The morphology of the polymer matrix can be controlled. The use of catalytic reactions in place of the usual organic synthesis will shorten the reaction time and the amount of the reaction steps. Polymer-supported transition metal complexes have started to be looked at as good alternative to typical inorganic carriers. The main advantage of polymer supports is the chemical, physical and morphological structure of these materials and its influence on the catalytic properties of the metal complex immobilized on it. The use of catalysts based on epoxy supports reduce the amount of waste and pollution produced by the industry. Simple synthesis technology, high availability, and thus the low price of a wide range of epoxy resins causes that estimated production costs of the proposed materials are small.

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