



Full paper/Mémoire

Palladium complex catalyst immobilized on epoxy support under supercritical conditions

Natalia Bączek, Krzysztof Strzelec*

Institute of Polymer and Dye Technology, Faculty of Chemistry, Lodz University of Technology, Stefanowskiego 12/16, 90-924 Lodz, Poland

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ABSTRACT

The aim of this research was to obtain a new-generation complex catalyst under supercritical carbon dioxide. A new complex catalyst based on epoxy resin cured with multifunctional polythiourethane was prepared. The use of polythiourethane as a hardener allowed us to introduce linking groups into the structure of the polymer without further functionalization of the resin. Additionally, the use of supercritical CO₂ enabled a more accurate and better distribution of the metal complex in the polymer matrix. The presence of the functional groups allowed us to obtain a catalyst wherein the metal centers had a different electronic structure and various degrees of oxidation, so that such a system was characterized by its high selectivity. The catalytic properties of the prepared catalysts were tested in the hydrogenation reaction. Research methods like time-of-flight secondary-ion mass spectrometry (ToF-SIMS), infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and nitrogen BET surface area measurements were used to characterize polymeric support and heterogenized catalysts.

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1. Introduction

Recently, there has been a growing interest in exploring transition metal complex catalysts immobilized on polymeric organic matrices. Polymer-supported transition metal complexes have started to be looked at as good alternatives 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 them. The use of epoxy resins as carriers of catalysts has been limited so far to the use of the metal complex as the polymerization initiator and the precursor of the catalytic centres in the cured resin [1,2] and to the application of various matrices functionalized with epoxy groups for the immobilization of proteins and enzymes to

improve their biocatalytic properties [3]. Such resins were found to have a high capacity and selectivity towards metal-ion species. For example, a sulfur analogue of the glycidyl methacrylate resin was synthesized by Moore et al. [4], in which the oxirane group was replaced by a thiirane ring. The ring-opening reaction of the thiirane group with amines or other nucleophiles generates a thiol group at the β -carbon atom. Such immobilization of ligands produces ion-exchange resins that may be used in wastewater treatment and in the regeneration of metal salts in industrial processes. In these ion-exchange resins, not only the metal binds to the ligand, but also the thiol group takes part in metal-ion binding, thereby acting as additional donor site. Crudden et al. showed that thiol-functionalized mesoporous silicates are efficient Pd scavengers and that the resulting Pd-encapsulated materials catalyze the Suzuki–Miyaura and Mizoroki–Heck coupling reactions with virtually no leaching of Pd. Several heterogeneity tests were performed on the catalyst under Suzuki–Miyaura conditions and indicate that the main part

* Corresponding author.

E-mail address: krzysztof.strzelec@p.lodz.pl (K. Strzelec).

of the catalysis (> 95%) occurs on the support via a truly heterogeneous catalyst. Studies are ongoing to determine the structure of the catalyst and the scope of its activity [5]. Magnetic resins with amine and mercaptan as chelating groups were prepared by suspended condensation polymerization of 2-chloroethoxymethyl thiirane with diamines. The resins show a high affinity for noble-metal ions and Hg(II), and predominantly adsorbed Pd(II) or Hg(II) with Cu(II), Zn(II), and Mg(II) coexisting [6].

In our earlier works, we proposed a similar approach and used thiol-functionalized epoxy resins as coatings for magnetic cores in encapsulation processes. This novel type of supports for metal complex catalysts can be easily separated by the use of a magnetic field. Our experiments have shown that the microporous structure of the polymer supports in the hydrogenation of cinnamaldehyde seems to have higher impact on the reaction activity and selectivity as compared with the influence of the chemical structure of the supports. The morphology parameters, such as pore-size distribution and specific surface area depends on the type of thiol used as resin hardener [7].

In recent years, $scCO_2$ had many applications in many fields of chemistry. Supercritical fluids have a unique and valuable potential for the enhanced processing of many materials. The applications of supercritical fluids to polymer processing are known. The ability of supercritical carbon dioxide to swell and plasticize polymers is crucial to the impregnation, extraction, and modification of polymeric materials [8]. Supercritical fluid dyeing technology has received attention in the textile industry due to increasing environmental concerns. The solubilities of three novel disperse azo dyes in supercritical carbon dioxide were measured. The results show that this method is very promising for the development of supercritical processes for dyeing applications based on these dispersed dyes [9]. A thin film of polymer was fabricated on a functionalized silicon wafer through self-assembled monolayers (SAMs) of perfluorophenyl azide derivatives (PFPA-silane) with covalent bonds by photochemical reaction. The SAMs were formed in supercritical carbon dioxide and the immobilization of polymers was performed by UV irradiation. The results indicate that $scCO_2$ is a good solvent for silylation reactions, better than common organic solvents such as toluene [10]. Supercritical fluids allow the synthesis of many types of particles since the solvent's chemical and physical properties can be varied with temperature or pressure, both of which can affect the degree of supersaturation and nucleation. Hakuata reported methods for the formation of fine particles using supercritical fluids CO_2 and water [11]. Carbon dioxide in its liquid or supercritical state ($scCO_2$) has a prodigious potential as an environmentally benign reaction medium for sustainable chemical synthesis. Since the mid 1990s, rapidly increasing research efforts have shown that $scCO_2$ can replace conventional and potentially hazardous solvents in a wide range of processes. There is also increasing evidence that the application of $scCO_2$ can broaden the scope of catalytic synthetic methodologies [12].

Herein, we reported the synthesis of some efficient heterogenized palladium catalysts based on supports

prepared from epoxy resin cured with thiol-terminated polythiourethane. These novel effective curing agents were synthesized from low-molecular-weight di- and multi-functional mercaptans and diisocyanates [13]. The oligomeric polythiourethanes, apart from their good curing characteristic of epoxides, allow one to introduce new binding ligands into the structure of polymers. The immobilization of the homogeneous catalyst was carried out under supercritical conditions. The use of supercritical CO_2 will enable a more accurate and better distribution of the metal complex in a polymer matrix. The activity of these new catalysts was checked in the hydrogenation reaction.

2. Experimental

2.1. Materials

As epoxy resin, a high-purity bisphenol A diglycidylether D.E.R.TM332 (DER), epoxy equivalent 170 (viscosity 4000–6000 mPa·s at 25 °C), The Dow Chemical Company, USA, was used. A multifunctional polythiourethane hardener (MPTU) was prepared by the reaction of hexamethylene diisocyanate (HDI) and pentaerythritol tetrakis (3-mercaptopropionate) (SIGMA) in excess molar quantity (by 2 moles) using a previously reported method [13]. Homogeneous catalyst $PdCl_2(PhCN)_2$ was prepared from $PdCl_2$ (Sigma, 99%) and benzonitrile (Sigma, 99%) in petroleum ether (Sigma) [14]. Toluene (POCH), *trans*-cinnamylaldehyde (Aldrich), ethanol (POCH) were used for the hydrogenation reaction, without further purification.

2.2. Support preparation

Three grams of epoxy resin (DER) and 1.2 g of polythiourethane (MPTU) were placed in a flask and mixed until a homogenous consistency was obtained. The mixture was transferred into a Teflon[®] mold and cured at temperatures from 298 to 423 K over a time period of 1 h to 48 h. The cured resin was frozen by immersion in liquid nitrogen and mechanically ground to powder. The particle sizes were about 0.5 mm, which was determined by sieve analysis.

2.2.1. Preparation of the catalyst

On the prepared support, we immobilized the palladium complex $PdCl_2(PhCN)_2$ from a saturated toluene solution through a ligand-exchange process under supercritical conditions. The supercritical immobilization set-up is represented in Fig. 1. It is mainly composed of a 100 ml stainless steel autoclave equipped with a thermostat, a temperature controller and a pressure indicator. In a typical experiment, 0.5 g of the support and 15 ml of a saturated solution of the palladium complex were introduced into the glass tube, which was placed at the bottom of the autoclave. The autoclave was heated to the set temperature and filled with liquid CO_2 through a high-pressure pump until the desired pressure has been reached. The immobilization was carried out for 5 h at 300 K and at a pressure of 90 bar. The supercritical phase, containing the catalyst precursor, diffuses inside the polymer matrix during a pre-established impregnation

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