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Preparation of polymer anchored Pd-catalysts: Application in Mizoroki–Heck Reaction

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ABSTRACT

A series of polymer anchored Schiff bases were prepared from chloromethylated styrene–divinylbenzene copolymer beads and loaded with $PdCl_2$ to get air and water stable supported catalysts. The catalysts were characterized and utilized in Mizoroki–Heck reaction of aryl bromides and iodides.

1. Introduction

Development of chemical transformations utilizing environmentally compatible and safe methodologies has gained renewed importance. Many efforts are underway to modify the existing important reactions to meet ever increasingly stringent environmental norms. In this effort, immobilization of toxic metal complexes on polymer supports and explore their use in many reactions is of vital consideration [1,2]. The distinct advantage of polymer anchored metal catalysts in conventional reactions is of several folds: simple methods of immobilization, easy recoverability, reusability, effortless extraction, high activity, solvent compatibility, economy when costly metals are used etc. Some of the metals used for catalytic reactions are toxic or undesirable in sensitive products such as pharmaceutical intermediates where the use of heterogeneous catalysts can help to keep the levels of their contamination low and to the acceptable level. The concept of polymer supported metal complexes is widely explored by several researchers and the subject is extensively covered in the recent literature [3–9]. Since the first report by Merrifield on the concept of polymer supported peptide synthesis [10] several significant developments have taken place to use a host of polymeric materials as supports for synthesis and catalysis [11–18]. These include the use of soluble polymer supports [13,14], dendrimers [18,19], polysiloxane [20,21], self-supported polymeric catalysts [22], nano-particles [23], metals loaded on clays and zeolites [24,25], metal oxides, mesoporous materials [7], etc.

Polymer prepared by crosslinking of polystyrene and divinylbenzene remains an easily available and well studied support for facile functionalization and hence a support of choice by many groups of researchers. In this paper we report our findings on the synthesis of polymer bound Schiff base ligands, their palladium complexes and applications of the Pd-loaded catalysts for Mizoroki–Heck coupling reaction [26]. There are a few reports on polymer bound phosphine ligands [27–29], but very few of phosphine free N,N type polymer attached Pd complexes have been developed for this reaction [30].

2. Experimental

2.1. Material

Chloromethylated poly(styrene–divinyl benzene) copolymer spherical beads (0.3–1.2 mm) with 5 or 8% crosslink were supplied by Ion-Exchange (India) Limited, Mumbai. Palladium chloride, 1,3-diaminopropane, 4,4′-diaminobiphenyl and iodobenzene were obtained from Aldrich and used without further purification. Styrene (Fluka) was distilled before use, 4-iodo anisole was prepared from 4-anisidine [31], and other chemicals and solvents of analytical grade were purchased from local suppliers.

2.2. Preparation of polymer anchored chelating ligand

Commercial sample of chloromethylated resin beads were first purified by soxhlet extraction with methanol to remove the sol-

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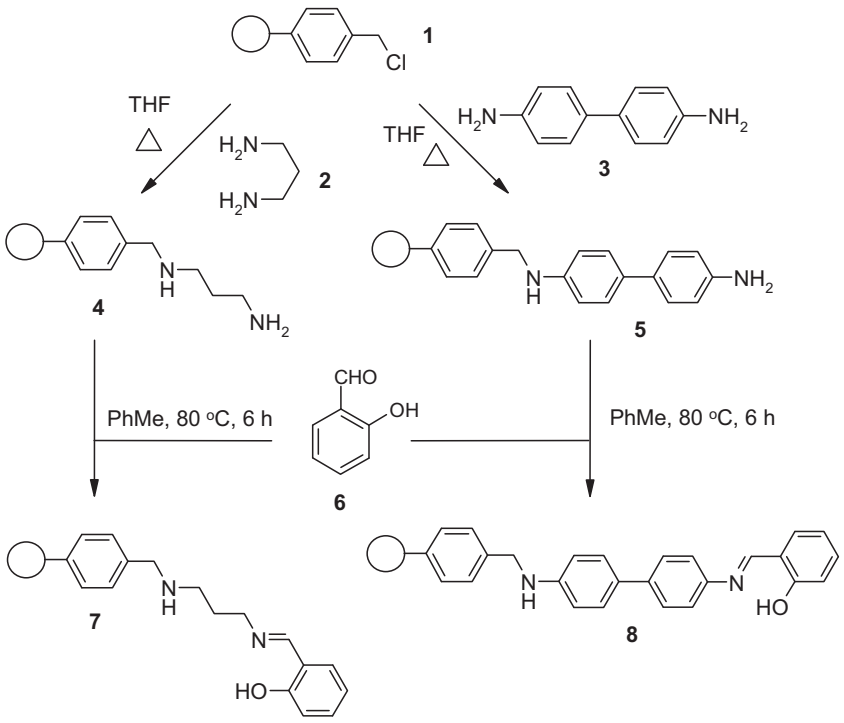

Scheme 1. Synthesis of polymer anchored Schiff bases.

uble impurities. Purified resin was then stirred for several hours with appropriate quantity of diamines, *viz* 1,3-diaminopropane **2** and 4,4′-diaminobiphenyl **3** dissolved in tetrahydrofuran such that one of the amino groups is alkylated and other remained free. The beads of product **4** or **5** obtained from the two reactions were separated and washed carefully with the same solvent and then successively with methanol, deionised water, dioxane and again with dry methanol and dried at 50 °C under reduced pressure. Having established the presence of amino group by IR spectral analysis samples of **4** and **5** were heated with excess of salicylaldehyde **6** in toluene at 80 °C [32]. The formation of Schiff base anchored onto the polymer **7** and **8** was established by analytical and IR analysis.

2.3. Loading of Pd(II) on the polymer anchored ligand

The polymer beads of **7** or **8** were kept in ethyl alcohol for one hour in a round bottom flask. These were then treated with 1% (w/v) solution of $PdCl_2$ in the same solvent, initially at 50 °C for 45 min with occasional shaking and then left on mechanical shaker for 15 days at room temperature. After this time the color of beads changed to brown giving a preliminary indication of loading of the metal on the resin giving polymer anchored Pd-catalyst beads. The beads were separated, washed with ethyl alcohol and dried under reduced pressure at 60–65 °C for 24 h. By this procedure the following polymer anchored Pd-catalysts were prepared: **A-1** and **B-1** with 5% crosslink and **A-2** and **B-2** with 8% crosslink, where **A-1** and **A-2** were obtained from **7** and **B-1** and **B-2** are from **8**.

The present study involves characterization and screening of these four catalysts for the Mizoroki–Heck reaction of aryl halides with styrene to prepare stilbene derivatives.

2.4. Analysis of catalyst

Elemental analysis of the polymer anchored Schiff bases and the corresponding Pd-catalysts were carried out on Coleman Analyzer. The metal contents of the polymer anchored catalysts were estimated using Perkin-Elmer Atomic Absorption Spectrometer, Model Zeeman ZL-4100, for which a known weight of catalyst was digested with conc. HCl and then diluted to constant volume for the analysis. Surface area of the polymer beads before and after complexation with metal was determined using the BET method with a Carlo-Erba Surface Area Analyzer. The IR spectra in the range of 50–4000 cm^{-1} were recorded on a Nicolet Manga-550 Spectrophotometer. Thermogravimetric analyses of the catalysts were carried out on Shimadzu DT-30 Analyzer at a heating rate of 10 °C min^{-1} up to 600 °C under the atmosphere of nitrogen. Diffuse reflectance spectra (200–400 nm) were recorded on a Shimadzu UV-240 instrument using optical grade $BaSO_4$ as the reference. Scanning electron micrographs of the catalysts and the supports were taken on Jeol JSM-T 300 instrument. Swelling behavior of the freshly prepared catalysts in polar and non-polar solvents and their bulk densities at 27 °C were measured as described previously [33].

The structures of various stilbenes obtained by catalytic coupling reaction were established by comparing the m.p. with known or reported values and H NMR spectra.

2.5. Procedure for catalytic Heck reaction

The reaction of aryl halide and olefin, usually attached with an electron withdrawing group in presence of Pd-catalyst and a suitable base, Mizoroki–Heck reaction, is an extremely important method of synthesis of substituted stilbene and cinnamic acid derivatives [34–36]. Separation of the used catalysts for further reactions is crucial for viable applications. Also the contamination of palladium in the sensitive products becomes a matter of concern. The variants of catalysts **A** and **B** were taken in solvent and allowed to swell for 30 min, and charged with the reagents for Mizoroki–Heck reaction. Two solvent systems were identified: i. water with small quantity of cetyltrimethylammonium bromide (CTAB) as promoter and ii. dimethylacetamide (DMA) for this reaction, while the third solvent toluene was not very effective. The mixture is heated for several hours and the progress of reaction