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Diamine functionalized gel-type resin as a support for palladium catalysts: Preparation, characterization and catalytic properties in hydrogenation of alkynes

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ABSTRACT

Gel-type resin (FCN) obtained as a result of copolymerization of glycidyl methacrylate (20 mol%), styrene (77 mol%) and ethylene glycol dimethacrylate (3 mol%) and functionalized by amine groups is studied as the support for Pd-catalysts (0.5–2 wt% Pd). Pd/FCN catalysts are characterized by number of techniques (FTIR, UV–Vis, XPS, SEM and HRTEM) and tested in the hydrogenation of alkynes, 2-butyne-1,4-diol (B3-D) and phenylacetylene (Phc). Catalysts are prepared by incorporation of palladium to the swollen particles of FCN resin using THF solution of $Pd(OAc)_2$. In these conditions N and carbonyl groups of FCN polymer are involved in the bonding of Pd^{2+} ions. This leads to decrease in swelling ability of polymer mass due to “crosslinking” of the polymer via Pd^{2+} ions. Since the polymer-bound Pd species are only partially reduced under hydrazine treatment the reduced Pd/FCN samples swell less than pure FCN. In the reduced Pd/FCN samples, only at the lowest Pd-loading amounted to 0.5 wt% Pd, very well dispersed Pd-nanoclusters appear. At higher Pd content within the range 1–4 wt% Pd, the particles of Pd of size within the range 4–28 nm are formed and in all the samples the particles 8–16 nm in size predominate. In these catalysts, partial aggregation of Pd-nanoparticles proceeds, especially when the loading of Pd is higher than 1 wt%. The activity/selectivity behaviour of Pd/FCN catalysts is determined by the size of Pd-particles and swelling ability of polymer matrix under the catalytic run. In the presence of highly expanded catalysts with low Pd content, 0.5–1 wt% Pd, the alkynes substrates, B3-D or Phc are hydrogenated to alkene with selectivity 91–92% up to high alkynes conversion (90%). The suppression of alkene to alkane hydrogenation in the stage of alkynes is ascribed to high ability of Pd-centers to strong adsorption of alkyne substrate. It may also be related to steric hindrances of polymer in the vicinity of active Pd-centers caused by the swollen polymer network.

1. Introduction

Specific properties of polymers like hydrophobic/hydrophilic character, the presence of various functional groups, ability for swelling in reaction medium make these materials very attractive from the catalytic point of view. Moreover, frequently observed high ability of these organic materials for the stabilization highly dispersed metal nanoparticles makes polymers promising candidates as the supports for noble metals particles like Pt, Pd, Rh. Very advantageous influence of polymer matrix on reactivity of metallic centers, such as Pd, Pt has already been observed in various types of catalytic reactions, like oxidation, hydrogenation etc. [1,2]. This profitable role of polymers has been related to modification of Pd, Pt-centers reactivity

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due to the presence of structural units (like-N-, S-, O-heteroatom groups) of polymers. Moreover, polymer network may also exert the influence on the accessibility of reagents to active centers inside the polymer mass [3–5]. This latter effect can essentially influence the selectivity of reaction and this effect seems to be especially important in the case of gel-type polymers, exhibiting the ability for swelling in contact with reaction medium. Swelling of the polymer effectively separates the polymeric chains thus dramatically affecting the accessibility of reagents to the active centers. As a consequence, catalytic centers formed in functional resins act in the environment of swollen polymer gel, which is essentially different from the surface of conventional solid supported metallic catalysts [6,7].

Gel-type FCN resin studied in the present work consists of carbonyl and N-functional groups (Schemes 1 and 2). This resin is studied as the potential support for palladium catalysts. The object of the present work is to elucidate the nature of interactions between the functional groups of FCN polymer and palladium ions. Thus, present work can be treated as the initial step and the results of the work may serve as the basis for the preparation of FCN-supported palladium catalysts.

Changes in the structure of FCN resin resulting from the incorporation of Pd(II) ions have been investigated by FTIR, UV–Vis, XPS and DSC techniques. Electron microscope techniques (SEM and HRTEM) have served as complementary experimental tools for characterization the morphology of Pd-particles formed in reduced form of Pd/FCN samples.

The role of specific properties of FCN polymer in catalytic reactivity of Pd-centers is studied in the liquid phase hydrogenation of alkynes namely phenylacetylene (Phc) and 2-butyne-1,4-diol (B3-D) both are an example of consecutive hydrogenations of unsaturated triple C≡C bond to the double C=C and finally to the saturated C–C one. The former, hydrogenation of phenylacetylene is frequently studied as the model reaction the latter hydrogenation of B3-D (Scheme 3) is a reaction of industrial relevance [8–10].

Supported palladium catalysts are widely studied in the hydrogenation of unsaturated triple C≡C bond in alkynes to the double C=C one in alkenes. On commonly used Pd-catalysts, the selectivity to olefinic molecule is frequently reduced due to the formation of fully saturated molecule already in the stage of unsaturated triple C≡C bond hydrogenation. In order to reach selective formation of alkene an appropriate electron-geometric properties of Pd-centers are required [11]. Therefore to produce selectively olefinic products various attempts have been undertaken such as the additive of N-bases like amines, quinoline to the hydrogenated solution or modification of Pd-catalysts by the metals additives like Pb, Zn. However, N-groups-containing polymers such as heterocyclic polyamides [12], polyvinylpyridines [13], oligoaramides [14] have been found to have favourable effect on the performance of Pd-catalysts in hydrogenation of numerous alkynes by facilitating the selectivity towards the desired alkene. In this context, studies are undertaken in the present work using functionalized by N-groups gel-type FCN resin. One can expect that in the case of FCN gel-type resin, not only the presence of N-groups but also swelling of polymer mass, both may exert the effect on the activity and the selectivity of Pd/FCN catalysts.

2. Experimental

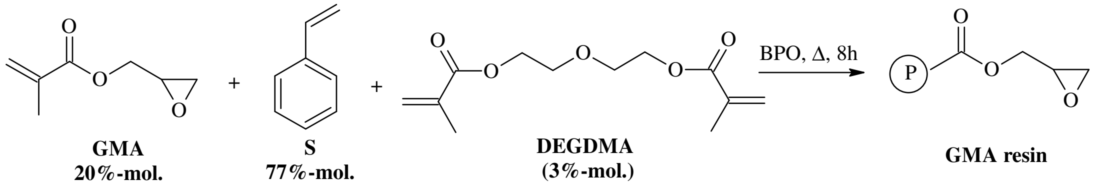
2.1. Synthesis of FCN resin

Monomers glycidyl methacrylate (GMA), styrene (S) and diethylene glycol dimethacrylate (DEGDMA) were purchased from Aldrich. They were additionally purified from polymerization inhibitors by extraction with 5 wt% NaOH in 20 wt% NaCl solution. Other reagents and solvents were used as received.

The gel-type FCN resin was prepared by two stage procedure (Schemes 1 and 2). In the first stage of preparation (Scheme 1) GMA resin was obtained by suspension polymerization of the mixture of glycidyl methacrylate (20 mol%), styrene (77 mol%) and diethylene glycol dimethacrylate (3 mol%) according to previously reported procedure [15]. The obtained GMA resin (loading of epoxy groups about 1.3 mmol per gram [15]) was in the form of spherical particles. Results of elementary analysis of GMA resin are: 78.007 wt% C, 7.242 wt% H, 14.751 wt% O. They show that the content of methacrylic monomers in the obtained GMA resin is higher than it could result from the composition of monomers on the stage of their copolymerization.

The beads fraction of GMA resin with diameters within the range 150–250 μm was used for the functionalization by ethylene diamine (EDA) (Scheme 2).

In order to introduce N-groups the GMA resin was reacted for 24 h with five-fold excess of ethylene diamine in DMF medium (10 cm^3 per gram of the resin) at 80 °C (Scheme 2). The modification was carried out in a thermo-



BPO – benzoil peroxide

Scheme 1. Preparation of GMA resin.