



Transitional metals immobilized by coordination on aminophosphonate functionalized copolymers and their catalytic properties



Adriana Popa^a, Ramona Ene^b, Diana Visinescu^b, Ecaterina Stela Dragan^c, Gheorghe Ilia^a, Smaranda Iliescu^a, Viorica Parvulescu^{b,*}

^a Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

^b "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, 060021 Bucharest, Romania

^c "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, 700487 Iasi, Romania

ARTICLE INFO

Article history:

Received 19 September 2014

Received in revised form 29 July 2015

Accepted 30 July 2015

Available online 1 August 2015

Keywords:

Polymer supported catalysts
Aminophosphonate functionalized copolymer
Cu(II) complexation
Mn(II) immobilization
Catalytic oxidation

ABSTRACT

Aminophosphonate functionalized copolymers were obtained as supports for transition metals immobilization in order to use them in catalytic applications. Styrene-divinylbenzene copolymer was functionalized with aminophosphonate groups by Kabachnik–Fields reaction. TG, FTIR, UV–vis–NIR and XPS confirmed the functionalization of the surface of polymer and evidenced the ligand effect of aminophosphonate groups on metal cation properties. Two effects of the supports were evidenced on interaction with cation metals respectively catalytic activity: *ortho*- or *para*- position of amino and phosphonate groups and nature of amine radicals. The fragile equilibrium between the two antagonistic effects could explain the formation of copolymer-3d metal ions assemblies and also the absence of interaction between manganese cation and supports with *ortho* position of amino and phosphonate groups.

Catalytic properties of the obtained catalysts were evaluated in oxidation with hydrogen peroxide of organic compounds (anisole, cyclohexene, toluene, styrene, phenol). Turnover rate (TOF) values showed a higher activity, except oxidation of cyclohexene and phenol, for Cu catalysts with *para* isomer and *ortho*-Cl-C₆H₄ amine radical. Lower activity was obtained for Mn catalysts with similar supports. The recycled catalysts were still active after three times reuse, however, a high variation of the catalytic performance was evidenced for Mn catalysts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

α -Aminophosphonates, due to their structural analogy to α -amino acids, have been the subject of considerable interest [1]. Extensive investigations over the last twenty years have shown that they are of particular importance in biological and medical research [2,3]. In this respect, the uses of α -aminophosphonates as enzyme inhibitors, antibiotics and pharmacological agents, herbicides and haptents of catalytic antibodies are well documented [4]. The modification of polymers has also received attention in the last years. New materials were obtained by functionalization [5,6] or grafting of polymers [7–9] and diversity of their applications increased. The synthesis of modified polymers with phosphonic acid groups [10,11] phosphonate groups [12–15] and aminoalkylphosphonic

groups [16] is often mentioned in literature. The first one-pot synthesis of α -aminophosphonates has been achieved by the reaction of OH-phosphonate in the presence of lanthanide triflate [17] as the catalyst with imines generated *in situ* from aldehydes and amines in organic solvent. Since Merrifield reported the method of "solid-phase peptide synthesis" in 1963 [18], there has been an increased interest in the application of polymers as participants in catalysis [19–23], organic synthesis [24], environmental separation [25–30] and antibacterial agents [31–33]. Chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely employed macromolecular supports for heterogenization of homogeneous catalysts [34]. The polymer-supported catalysts have received wide attention because these materials offer advantages to the new catalytic systems like selectivity, recyclability and easy separation from reaction products leading to the operational flexibility [35]. The polymer-supported metal complexes showed higher catalytic activity in various chemical reactions such as oxidation [36,37], oxidative functionalization [38], hydrogena-

* Corresponding author.

E-mail address: vpirvulescu@icf.ro (V. Parvulescu).

tion [39] and acid catalysis processes [40]. For example, in oxidation of phenol and epoxidation of cyclohexene the supported catalysts showed low energy of activation than unsupported catalysts. This clearly suggested that polymer supports played a significant role in decreasing the energy of activation for these reactions in the presence of metal complexes [41].

The aim of this work was to obtain new catalysts by immobilization of Cu and Mn ions on functionalized copolymer supports. The surface of styrene-divinylbenzene copolymer was functionalized with aminophosphonate groups in order to highlight their effect on metals complexation and on catalytic properties of the obtained materials. The impregnation of transition metals on a chelating substrate like styrene-divinylbenzene copolymer functionalized with aminophosphonate groups is similar with an exchange or chromatographic processes [42,43]. Cu(II) and Mn(II) cations were selected for the chelating effect on them of aminomethylphosphonate groups [44] and influence of this process on catalytic properties of the supported complexes. The catalytic properties of Cu(II) and Mn(II) cations were evidenced in oxidation with hydrogen peroxide of the organic compounds [45–48]. Results obtained before [48] evidenced the influences of styrene-divinylbenzene copolymer functionalized surface on catalytic properties of the immobilized Cu(II) complexes. These properties were evaluated in oxidation with hydrogen peroxide of organic compounds (anisole, cyclohexene, toluene, styrene, phenol). New catalysts were obtained in order to emphasize direct effect of copolymer organic function as ligand of transitional metal cations on catalytic activity, selectivity and stability.

2. Experimental

2.1. Materials

Chloromethylated styrene-divinylbenzene copolymer (chloromethylated St-6.7%DVB copolymer), supplied by Puro-lite Victoria Romania, copolymer St-(6.7%DVB) grafted with aldehyde groups synthesized in our laboratory [47], 2-hydroxybenzaldehyde (Sigma-Aldrich, 98%), 4-hydroxybenzaldehyde (Merck, 98%), *N,N*-dimethylformamide (Sigma-Aldrich, 99%), propylamine (Fluka, 99%), ortho-chloroaniline (Loba Chemie, 98%), tetrahydrofurane (Sigma-Aldrich, 99%), tetraethylammonium iodide (Merck, 98%), potassium carbonate (Sigma-Aldrich, 99%), methanol, acetone ethanol, dichloromethane and diethyl ether (Chimopar, 99%), CuCl₂·2H₂O (Sigma-Aldrich, 99%), and MnCl₂·4H₂O (Sigma-Aldrich, 98%) were used as starting materials for the polymeric catalysts preparation.

2.2. Reactions of chloromethylated St-DVB copolymer with 2-hydroxy and 4-hydroxy-benzaldehyde

Chloromethylated St-DVB copolymer (14.22% Cl) was used as the starting material in all syntheses. The synthesis of St-DVB copolymers functionalized with 2-hydroxy and 4-hydroxybenzaldehyde under phase-transfer catalysis (PTC) conditions in solid-liquid-liquid (chloromethylated St-DVB copolymer/*N,N*-dimethylformamide/aqueous potassium carbonate (K₂CO₃ (30%)) was performed by previously described method [48]. Chloromethylated St-DVB copolymer (10 g) was soaked 24 h in *N,N*-dimethylformamide (DMF 40 mL) in a 250 mL round bottom flask. After separation of DMF, the swollen copolymer was treated with (9.8 g) 4-hydroxybenzaldehyde (or 2-hydroxybenzaldehyde), (0.2 mmol) of tetraethylammonium iodide and aqueous K₂CO₃ (30%) (100 mL). The molar ratio of chloromethyl groups: 4-hydroxybenzaldehyde (or 2-hydroxybenzaldehyde) was 1:2. The mixture was maintained under stirring for 18 h at 95 °C. After

cooling, the polymer beads were separated by filtration, washed with methanol (3 × 20 mL), distilled water (3 × 20 mL), acetone (3 × 20 mL) and finally with diethyl ether (3 × 20 mL) and dried at 50 °C for 24 h.

St-DVB copolymer functionalized with 2-hydroxybenzaldehyde (2.79 mmoles –CHO/gram of copolymer (B2)) or St-DVB copolymer functionalized with 4-hydroxybenzaldehyde (2.94 mmoles –CHO/gram of copolymer (B3)) were obtained.

2.3. Synthesis of aminophosphonates grafted on macromolecular substrates and immobilization of transition metals

Four grams St-DVB copolymer (2.79 mmoles –CHO /gram of copolymer (B2) or 2.94 mmoles –CHO /gram of copolymer (B3)) and tetrahydrofuran (THF 50 mL) were added to a 100 mL round bottom flask fitted with reflux condenser, mechanical stirrer and thermometer. The mixture was then maintained under stirring for 2 h at room temperature to allow the copolymer beads to swell. The molar ratio of –CHO groups:diethylphosphite:amine (propylamine, ortho-chloroaniline) was 1:1:1. The final mixture was maintained under stirring for 20 h at temperature of 60 °C. After cooling, the polymer beads were separated by filtration, washed with ethanol (3 × 20 mL), 1,2-dichloromethane (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried under a vacuum of 2 kPa at 50 °C for 24 h.

Immobilization of the metals was made by impregnation of dry styrene-divinylbenzene support functionalized with aminophosphonate groups with CuCl₂ and MnCl₂ aqueous solutions in conditions of maximum amount of metal obtained by adsorption isotherms. After one washing step, the impregnated particles were dried 10 h at 80 °C.

2.4. Characterization of the materials

The obtained materials were characterized by Fourier transform infrared spectroscopy (Shimadzu FTIR), Ultraviolet-Visible-Near Infrared spectroscopy (Jasco V-570-(UV-vis-NIR)), scanning electron microscopy (Philips XL-20, FEI Quanta 3D FEG) and atomic absorption spectrophotometry (Spectra AA-220 Varian spectrophotometer). Thermal properties of the aminophosphonates grafted on crosslinked macromolecular substrates were characterized through thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a TGA/SDTA 851-LF1100—Mettler apparatus at a heating rate of 10 °C/min under N₂ atmosphere and temperature in the range 20–600 °C.

The phosphorus content of the polymer-supported aminophosphonates was obtained by adsorption in water of the P₂O₅ from a sample of the product precisely weighed and burnt out in an oxygen atmosphere [13,32]. The obtained solution was titrated with an aqueous solution of (NH₄)₂Ce(NO₃)₆ 0.005 M in the presence of Eryochrome Black T as indicator.

The apparent density (ρ_{ap}) was determined using a mercury pycnometer at 1.333×10^{-2} Pa. The specific density (ρ_r) was measured in *n*-heptane. The specific surface area (S_{sp}) was determined by the nitrogen adsorption at the boiling temperature of liquid nitrogen, by the Haul-Dümbgen method on a Ströhlein Area Meter apparatus. The average pore radius was calculated using the following equation (cylindrical shape of pores being assumed):

$$r_p = \left(\frac{2V_p}{S_{sp}} \right) \times 10^3 (\text{nm}) \quad (1)$$

where $V_p = (1/\rho_{ap}) - (1/\rho_r)$, pore total volume, mL/g.

The catalytic properties of polymer supported metals were evaluated in oxidation with hydrogen peroxide of the organic substrates (anisole, cyclohexene, toluene, styrene, phenol). The reactions were carried out in the thermostated glass mini reactors

Download English Version:

<https://daneshyari.com/en/article/64883>

Download Persian Version:

<https://daneshyari.com/article/64883>

[Daneshyari.com](https://daneshyari.com)