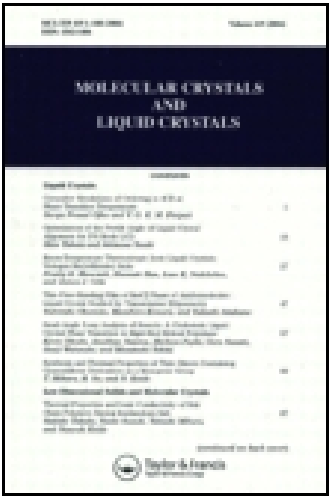

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New Poly(organophosphazene) - Supported Cobalt or Copper (II) Catalysts for the Oxidation of Alkenes

E. Błaż [a] & J. Pielichowski [a]

[a] Department of Polymer Chemistry and Technology , Cracow University of Technology , Poland

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New Poly(organophosphazene) - Supported Cobalt or Copper (II) Catalysts for the Oxidation of Alkenes

E. Błaż and J. Pielichowski
Department of Polymer Chemistry and Technology, Cracow University of Technology, Poland

Polymer-supported heterogeneous catalysts in form of complexes of poly[bis(pyridine-2-oxy)phosphazene] with cobalt(II) or copper(II) acetate were synthesized. The catalysts were prepared by a three-step reaction procedure. First, poly(dichlorophosphazene) was synthesized by thermal polymerization of cyclic trimer of hexachlorocyclotriphosphazene. In the second stage, the poly(dichlorophosphazene) structure was converted into the 2-hydroxypyridine by a nucleophilic substitution reaction. The last stage of the catalyst synthesis was the reaction of poly[bis(pyridine-2-oxy)phosphazene] with cobalt acetate or copper acetate. FTIR, ^{31}P NMR, AAS, BET, SEM, SEM-EDS and TG were employed for characterization of the obtained catalysts. The complexes were applied as heterogeneous catalysts in oxidation of dodecene, indene, limonene in the presence of molecular oxygen in acetonitrile (as solvent) at 60°C, using isobutyraldehyde as an "oxygen transfer" agent. Oxidation reactions of aliphatic and aromatic hydrocarbons let to formation of epoxides or ketones with good yield and high selectivity.

Keywords: alkenes; oxidation; polyphosphazene-based catalysts

INTRODUCTION

Catalytic oxidation is an area of particular significance for homogeneous catalysis as most of industrial processes involving catalytic oxidation are practiced in the homogeneous phase. However, the problems related to corrosion, decomposition on the reactor walls, recovery of the catalyst from the reaction mixture and its reuse are limitations in homogeneous catalytic processes. The present day stringent ecological standards also require attention to the environment friendly methods. Recovery of the catalysts and their reusability can

Address correspondence to J. Pielichowski, Department of Polymer Chemistry and Technology, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland. E-mail: pielich@usk.pk.edu.pl

be simplified if a homogeneous complex is heterogenized by supporting on an insoluble support. Polymers used as support have gained attention as they are inert, non-toxic, non-volatile, insoluble and often recyclable [1].

Thus, search for viable polymer-supported catalysts has gained attention in industry as well as in chemical laboratories [2,3].

The aerobic epoxidation of alkenes with transition metal catalysts has been widely studied over the past decade. One of the well-known methods of alkene epoxidation in homogeneous system is the Mukaiyama procedure, where substrate is epoxidized using a transition metal complex as a catalyst, molecular oxygen as an oxidant and an aliphatic aldehyde as a co-reactant [4]. Transition metal complexes, such as Schiff's base complexes, are also suitable for the aerobic epoxidation of alkenes with a co-reacting aldehyde. For example, cobalt (II) Schiff's bases give good results; however, these catalysts are rather not selective for epoxidation [5,6].

It has been reported in the literature that the epoxidation of alkenes by various oxidants can proceed very efficiently when a polymer-supported catalyst is used. It offers several advantages in preparation procedures. The polymer is very stable (in the meaning of thermal properties) even in the oxidative atmosphere [7].

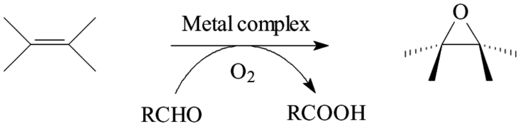
For example, the epoxidation of propene, octane and other alkenes using a polymer-bound $Mo^{VI}O_2(acac)_2$ catalyst was shown to be possible with yields up to 100% [8–10]. A Jacobsen-type manganese catalyst has been anchored to various polymer supports and has been used with different oxidants to make epoxides with 95% yield [11].

A polyaniline-supported cobalt(II) catalyst was prepared first by Pielichowski [12] and Iqbal [13] and was used for the aerobic epoxidation of alkenes. For example, a polyaniline-supported catalyst has been used for epoxidation of *trans*-stilbene with very high yield and selectivity [14,15].

More recently, polystyrene-bound nickel complexes have been synthesized by Han and Lei [16]. These catalytic systems showed high activity in the aerobic epoxidation of cyclohexene.

In recent years molecular oxygen has received much attention as a cheap, clean and readily available oxidant. For instance, Mukaiyama and co-workers have reported that molecular oxygen can be used as the terminal oxidant in the epoxidation of alkenes with an aldehyde or primary alcohol as coreactant and a metal β-diketonate as a catalyst [17,18]. The oxidation scheme is shown below (Scheme 1).

In our current studies, we have focused on polyphosphazenes that form one of the largest and most diverse classes of inorganic backbone polymer systems. Both linear polymers and cyclic phosphazene



SCHEME 1 Oxidation reaction of alkene.

monomers can be functionalized with a broad range of organic substituents. The most widely studied phosphazene polymer systems have a linear backbone of alternating phosphorus and nitrogen atoms with two organic groups linked to each phosphorus atom. Several hundred different polymers of this type are known, with properties that range from tough hydrophobic elastomers to water soluble and biodegradable polymers [19–21].

The modified polyphosphazenes are good candidates as catalysts for the oxygenation of organic compounds. Thus, in this paper, we report novel polyphosphazenes-supported cobalt (II) and copper (II) catalysts that were then tested in dodecene, indene and limonene oxidation reactions.

EXPERIMENTAL

Materials

The following materials were used in this work:

- hexachlorocyclotriphosphazene (HCPT) (pure, Riedel-de-Haën, USA)
- 2-hydroxypyridine ($>99\%$), sodium hydride 60% oil dispersion, cobalt(II) or copper(II) acetate tetrahydrate (99,9%) (Aldrich Chemical Co., USA)
- tetrahydrofuran (max. 0,005% H_2O, puriss, stabilized, Riedel-de-Haën, USA)

PREPARATION OF CATALYSTS AND THEIR USE

In the current work we present synthesis of novel polymeric catalysts and oxidation reactions that represent their catalytic properties. There are three stages of the catalysts synthesis:

(1) Polymerization of phosphonitrilic chloride trimer

Hexachlorotriphosphazene (2 g) was placed in a sealed ampoule and heated in a furnace at 240°C until the clear melted mixture became highly viscous but still slightly mobile. The ampoule was opened and only linear polymer $(NPCl_2)_n$ was dissolved in dry toluene.

(2) Substitution reaction, precipitation, and purification of the crude product

2-Hydroxypyridine (0,017 mol) and sodium hydride (0,9 g) were dissolved in 50 ml of dry THF. Next, 1 g of poly[di(chloro)phosphazene] in 10 ml of dry toluene was added and a small amount of catalyst – tetrabutylammonium bromide (TBAB), was added. The reaction mixture was refluxed for 48 hours. The polymer was isolated by precipitation with water. The reaction yield ranged from 70–80%.

The obtained product was identified by FT-IR and ^{31}P NMR:

IR (KBr), cm^{-1}: 3064 (ring OC_5H_4N); 1587(CC), 1470(CN) i 1431 (OC_5H_4N);

1215, 1185 (νPN); 1280 (νC–OP); 1046 (νP–OC); 900 i 951 (δPOC);743 i 785 (δPNP)

^{31}P NMR (DMSO): 7.72 ppm ($[NP(OC_5H_4N)_2]$ units)

(3) Preparation of poly[bis(pyridine-2-oxy)phosphazene] complexes with metal salts – cobalt or copper acetate

Poly[bis(pyridine-2-oxy)phosphazene] (0,5 g) and cobalt or copper acetate (II)(1g) were added into 50 cm^3 of acetonitrile. The mixture was stirred for 48 h at room temperature. Next, the catalysts were filtered off from reaction mixture and washed several times with acetonitrile. The catalysts were dried and kept in a desiccator; they were denoted as follows:

- poly[bis(pyridine-2-oxy)phosphazene] + cobalt acetate–Poly-2-POP-Co
- poly[bis(pyridine-2-oxy)phosphazene] + copper acetate–Poly-2-POP-Cu

(4) The oxidation of hydrocarbons in the presence of the catalysts

In order to check activity of the prepared catalysts, several reactions were carried out. In a typical procedure catalyst (30 mg), acetonitrile (30 mL) and substrate (2 mmol) were placed in a reactor. The mixture was heated up to 60°C, stirred with magnetic stirrer and bubbled with molecular oxygen. 2-methylpropanal was added (6 mmol) to reaction mixture. It worked as a reducing agent and as a co-catalyst. The reactions were carried out under atmospheric pressure. During the reaction, samples were drawn and dissolved in acetone. Then the conversion ratio of hydrocarbon into products was examined by GC-MS [22–26]. Finally, the organic layer was dried and the solvent was evaporated to give the desired product. All the products were characterized by analytical and spectroscopic techniques.

Dodecene, indene and limonene were subjected to the oxidation reactions.

RESULTS AND DISCUSSION

The complexes were characterized by AAS method. AAS measurements were done on apparatus Perkin Elmer Analyst 300. The samples of the catalysts were demineralized in 65% nitric acid and ionized using oxy-acetylene blow pipe. Next, the samples were analyzed using standard cobaltic or cupric cathode. The complexes were characterized by specific surface area using multilayer BET theory. The results are shown in Table 1.

The results show, that the catalyst poly-2-POP-Cu has large content of metal and better developed specific surface area in comparison to poly-2-POP-Co.

The thermal properties of the catalysts were investigated by TG method. Thermogravimetric analysis of the catalysts was performed on Netzsch TG-209 analyzer. The heating rate was 10 K/min from 30 to 600°C. Measurements were done in argon atmosphere (flow rate: 20 cm^3/min). The TG results are shown in Figure 1.

Both complexes decomposed in two steps. The first step of mass loss of about 10% for poly-2POP-Co and poly-2POP-Cu was at 181 and 167°C, respectively, and the mass loss of about 30% for poly-2POP-Co was at 592°C and 255°C for poly-2-POP-Cu. The amount of solid residue was 69,8 and 57,7%, respectively (Fig. 1). Generally, poly-2-POP-Co was more stable than poly-2-POP-Cu.

The decomposition degree at T30% for poly-2-POP-Co catalyst and T47% for poly-2-POP-Cu is decreased if the cobalt or copper acetate content is increasing (AAS data). This suggests, that incorporation of metals ions into the polymer matrix decreases its decomposition temperature. This is connected with the fact that the bonds in the complexes are weaker due to the coordination between the metal ion and the nitrogen atoms.

The specimen analyses were carried out using a HITACHI S-4700 field emission scanning electron microscope (SEM) equipped with a NORAN Vantage energy dispersive X-ray spectrometer (EDS). A focused electron beam was restored across the sample surface. The secondary or backscattered electrons produced were detected and used

TABLE 1 Total Co (II) and Cu (II) Content in Catalysts and Specific Surface

Catalysts	Content metal [mg metal/ 1 g sample]	Specific surface–BET [m^2/g]
Poly-2-POP-Co	65,2	85,8
Poly-2-POP-Cu	80,7	92,3

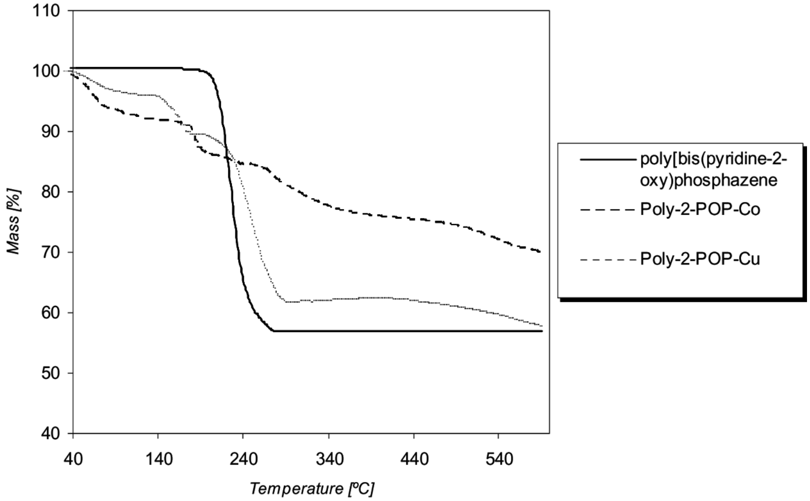


FIGURE 1 TG profiles of poly[bis(pyridine-2-oxy)phosphazene, poly-2-POP-Co and poly-2-POP-Cu.

to map the surface topography and compositional contrast based on the density differences. The X-rays emitted when the electron beam strikes a sample yielded information about the chemical composition of the sample surface (EDS). The analysis depth of EDS varied between 0.3 and 4.5 μm depending on the material analyzed and the primary beam energy. Two catalysts – poly-2-POP-Co and poly-2-POP-Cu – were examined by SEM/EDXS. Prior to analysis the catalyst samples were coated with conductive carbon films to a thickness of 20–30 nm.

Figure 2 shows surface images of poly[bis(pyridine-2-oxy)phosphazene]. Regular crystal forms can be observed.

The surface images of the catalysts are shown Figure 3. It can be seen that these heterogeneous catalysts created agglomerates with the size of the order of 20–30 μm and smaller about 5–10 μm. These agglomerates consist of many smaller lamellar crystal grains in case of poly-2-POP-Co and flaky-lamellar for poly-2-POP-Cu.

EDS spectra of the catalysts gave information about the relative contents of cobalt or copper on the sample surface and confirmed the efficiency of the doping process of poly[bis(pyridine-2-oxy)-phosphazene] with cobalt or copper acetate. The Co content was 4,9% for poly-2-POP-Co and Cu content was 8,1% for poly-2-POP-Cu (Fig. 4).

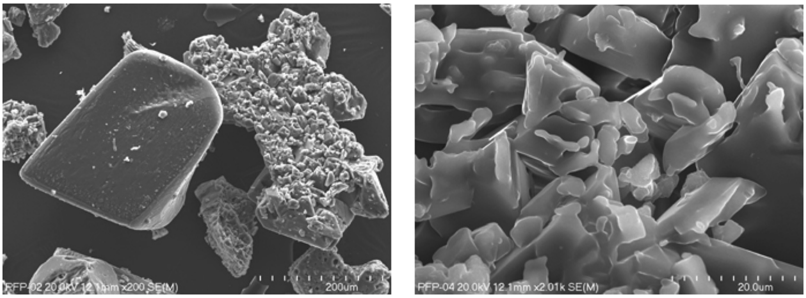
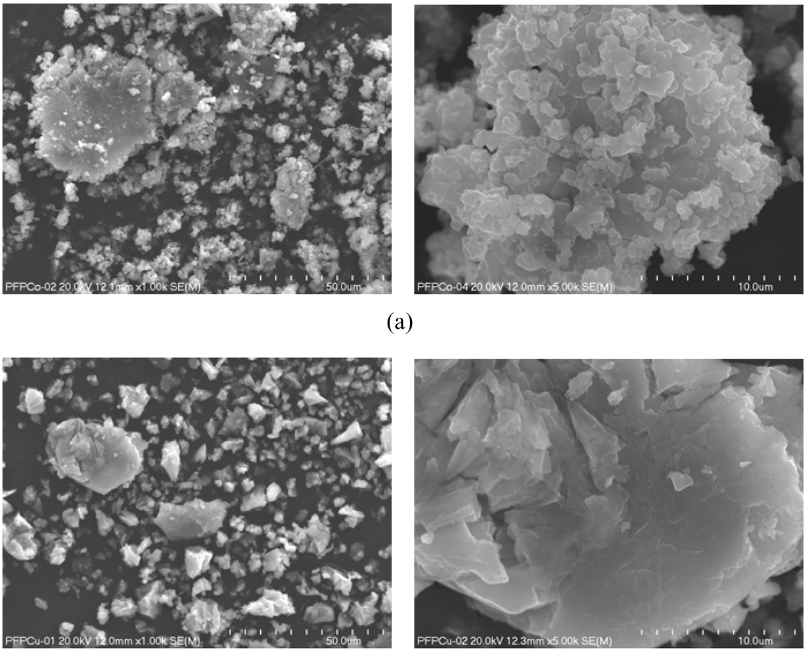


FIGURE 2 SEM images of poly[bis(pyridine-2-oxy)phosphazene.

Application of EDS spectroscopy coupled with SEM let us testing the surface distribution of chemical elements, for example metals, in the form of a surface map – Figure 5.

We observed that metal was spaced exactly on the catalyst surface. We can suggest that a chemical reaction take place between polymer and cobalt or copper (II) salt and only one compound was obtained.



(a)

(b)

FIGURE 3 SEM images of a) Poly-2-POP-Co, b) Poly-2-POP-Cu.

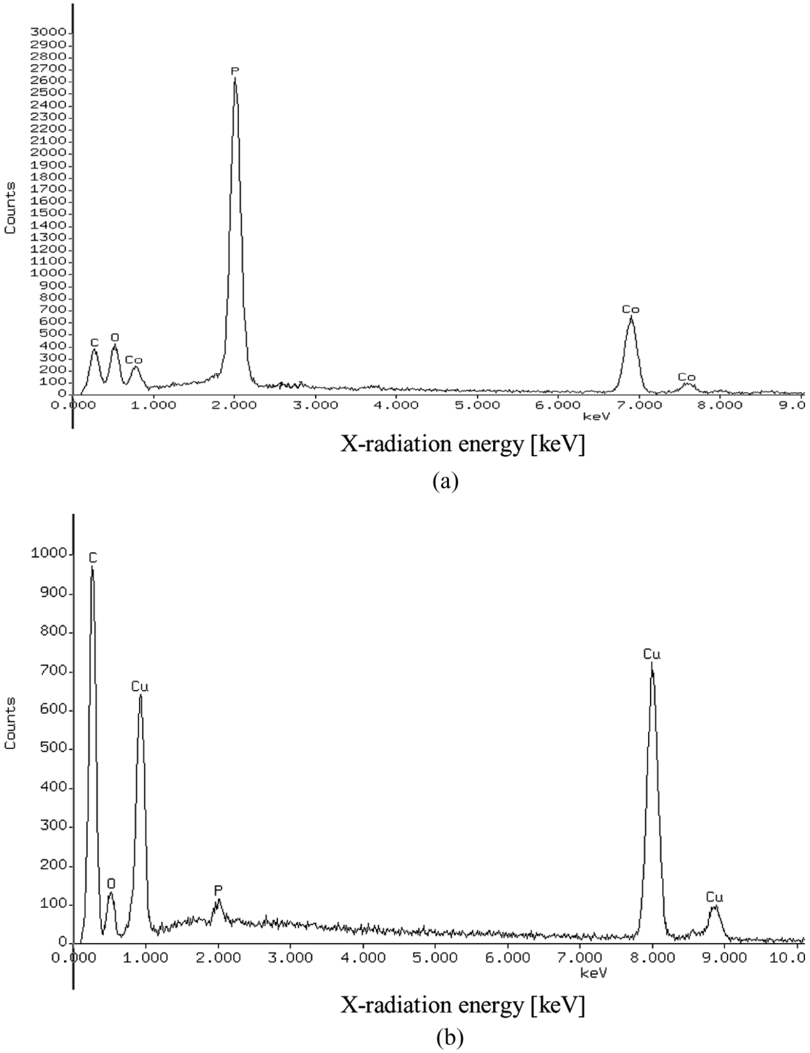


FIGURE 4 EDS spectrums of a) Poly-2-POP-Co, b) Poly-2-POP-Cu.

Catalytic Oxidation

Using these catalysts the aerobic oxidations of different organic compounds – dodecene, indene and limonene – have been carried out. The oxidation reactions are shown in Scheme 2. and the results are collected in Table 2.

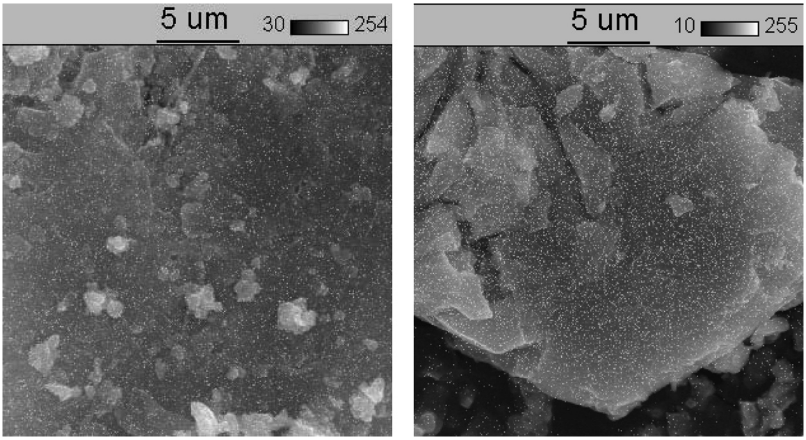
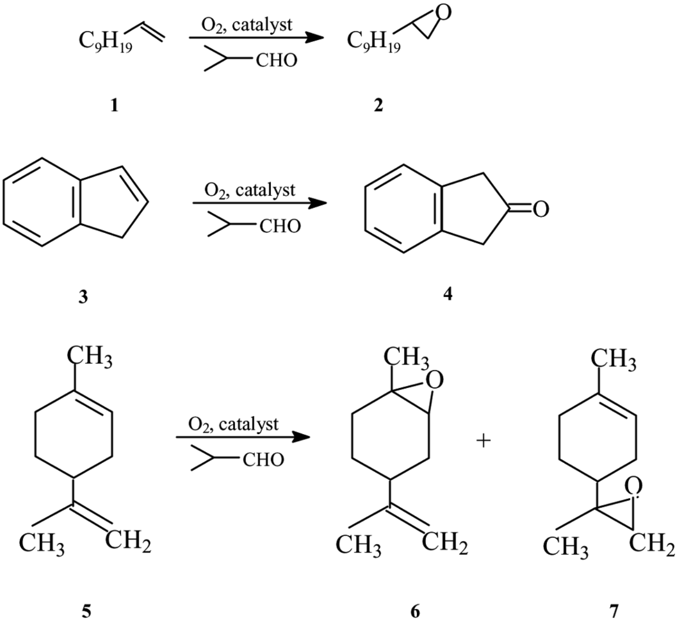


FIGURE 5 Metals distribution on poly[bis(pyridine-2-oxy)phosphazene; kobalt (left) and copper (right) respectively.

Limonene gives two epoxides and indene give ketone (1,3-dihydro-2H-inden-2-on) with very high selectivity and relatively high yield. The oxidation reaction of indene needs shorter time than oxidation



SCHEME 2 Oxidations of alkenes.

TABLE 2 Results of the Polymer – Supported Cobalt and Copper Catalysts Oxidation with Molecular Oxygen

	Products Yield [%] (time [h])		
Catalysts	2	4	6/7
Poly-2-POP-Co	30 (21)	97 (1)	75/20 (2)
Poly-2-POP-Cu	37 (20)	95 (1)	67/28 (1,5)

of limonene. The best results were obtained for poly-2-POP-Cu. Alkenes with terminal double bond show low reactivity therefore they need longer reaction time. Under these conditions 1-dodecene gives epoxide with very high selectivity. No changes in yield were observed when the same reactions were carried out longer.

Oxidation of double bonds proceeds easier when the double bond is activated by the presence of another group. In comparison, polymers-supported manganese porphyrin gave similar results as a catalyst in the oxidation reactions, but longer reaction time was necessary [27].

CONCLUSIONS

In conclusion, we have described the synthesis of polyphosphazene – based catalysts, which are very effective in oxidizing of alkenes under mild conditions. The main advantages of these catalysts are their efficiency, selectivity and simplicity of separation of the heterogeneous catalysts from the reaction medium by filtration. The oxidation reactions occur in relatively short time. Generally, poly(organo)phosphazenes can be considered as a new group of macromolecular oxidations catalysts, with advantageous properties.

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