EDYTA BŁAŻ, JAN PIELICHOWSKI*)

Cracow University of Technology
Department of Chemistry and Technology of Polymers
ul. Warszawska 24, 31-155 Kraków, Poland

New catalysts for oxidation reactions based on polyphosphazenes

RAPID COMMUNICATION

Summary — In the current work we describe the synthesis of novel polyphosphazene-based catalysts for oxidation reactions. The catalysts were prepared by a three-step reaction procedure. First, poly(dichlorophosphazene) was synthesized by thermal polymerization of the cyclic trimer of hexachlorocyclotriphosphazene. In the second stage, the poly(dichlorophosphazene) structure was converted into 2-aminopyridine and 3-aminopyridine by a nucleophilic substitution reaction. The last stage of catalyst's synthesis was reaction of poly(diaminopyridino)phosphazenes with cobalt acetate. IR, TG and AAS were employed for characterization of the catalysts obtained. Oxidation reactions of some alkenes were carried out using synthesized catalysts at atmospheric pressure in the presence of molecular oxygen. Epoxides and ketone were obtained as main products with very high yield and selectivity.
Key words: synthesis of polyphosphazenes, polyphosphazene complex of cobalt(II), polyphosphazene-based catalysts, oxidation of alkenes.

NOWE KATALIZATORY UTLENIANIA OLEFIN NA BAZIE POLIFOSFAZENÓW

Streszczenie — Przedstawiono trzyetapową syntezę nowych katalizatorów będących kompleksami kobaltu(II) z polifosfazenami (schemat A) oraz sprawdzono ich właściwości katalityczne przeprowadzając reakcje utleniania wybranych olefin. Pierwszy etap syntezy polegał na termicznej polimeryzacji cyklicznego trimeru — heksachlorocyklotrifosfazenu. Nastepnie do poli(dichlorofosfazenu) w wyniku nukleofilowej substytucji przyłączano 2-aminopirydynę lub 3-aminopirydynę. Ostatnim etapem tworzenia katalizatorów było kompleksowanie jonów kobaltu za pomocą poli(diaminopirydyno)fosfazenów. Otrzymane związki były charakteryzowane za pomocą metod IR, TG (rys. 1, tabela 1) i AAS. Zsyntetyzowane katalizatory zastosowano do utleniania *trans*-stilbenu, indenu i 1-decenu (schemat B). Reakcje utleniania prowadzono w obecności tlenu. Jako główne produkty otrzymano epoksydy i ketony a reakcje charakteryzowały się wysoką selektywnością i wydajnością (tabela 2).
Słowa kluczowe: synteza polifosfazenów, polifosfazenowe kompleksy kobaltu(II), katalizatory polifosfazenowe, utlenianie alkenów.

The aerobic epoxidation of alkenes with a transition metal catalyst has been widely studied over the past decade. One of the well-known methods of alkene epoxidation in homogeneous system is Mukaiyama procedure, where the substrate is epoxidized using transition metal complex as a catalyst, molecular oxygen as an oxidant and an aliphatic aldehyde as co-reactant [1]. Transition metal complexes, such as Schiff's base complex, 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 [2, 3].

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 the preparation procedures. The polymer is very stable (in the meaning of thermal properties) even in the oxidative atmosphere [4]. A polyaniline-supported cobalt(II) catalysts were prepared first by Pielichowski *et. al.* [5]. Bhaskar and Iqbal [6] used these catalysts for the aerobic epoxidation of alkenes. A polyaniline-supported catalyst has been used for epoxidation of *trans*-stilbene with very high yield and selectivity [7, 8].

In our current studies, we have focused on polyphosphazenes that form one of the largest and most diverse classes of inorganic backbone polymer systems. They show many interesting properties, such as hydrophilicity and hydrophobicity, bioinertia, bioactivity, conduc-

---

*) Author to whom all correspondence should be addressed; e-mail: pielich@usk.edu.pl

tivity, electroactivity, flame resistance and can also be used as catalysts, depending on the nature of the substituent [9—12].

Polyphosphazene catalysts take very little place among catalytic systems. Thus, in this paper, we report the novel polyphosphazenes supported cobalt(II) catalysts. These catalysts, based on polyphosphazenes with 2-aminopyridine and 3-aminopyridine, have been obtained and tested in *trans*-stilbene, indene and 1-decene oxidation reactions.

EXPERIMENTAL

Materials

The following materials were used in this work:

— hexachlorocyclotriphosphazene (HCPT) (pure, Riedel-de-Haën, USA),

— 2-aminopyridine, 3-aminopyridine (>99 %) and acetate cobalt(II) tetrahydrate (99.9 %) (all from Aldrich Chemical Co., USA),

— triethylamine (analytically pure, POCh, Gliwice, Poland),

— tetrahydrofuran (max. 0.005 % H_2O, pure, stabilized, Riedel-de-Haën, USA).

Preparation of catalysts

The general method of polyphosphazenes catalysts' synthesis is illustrated in Scheme A.

There are three steps of catalysts synthesis:

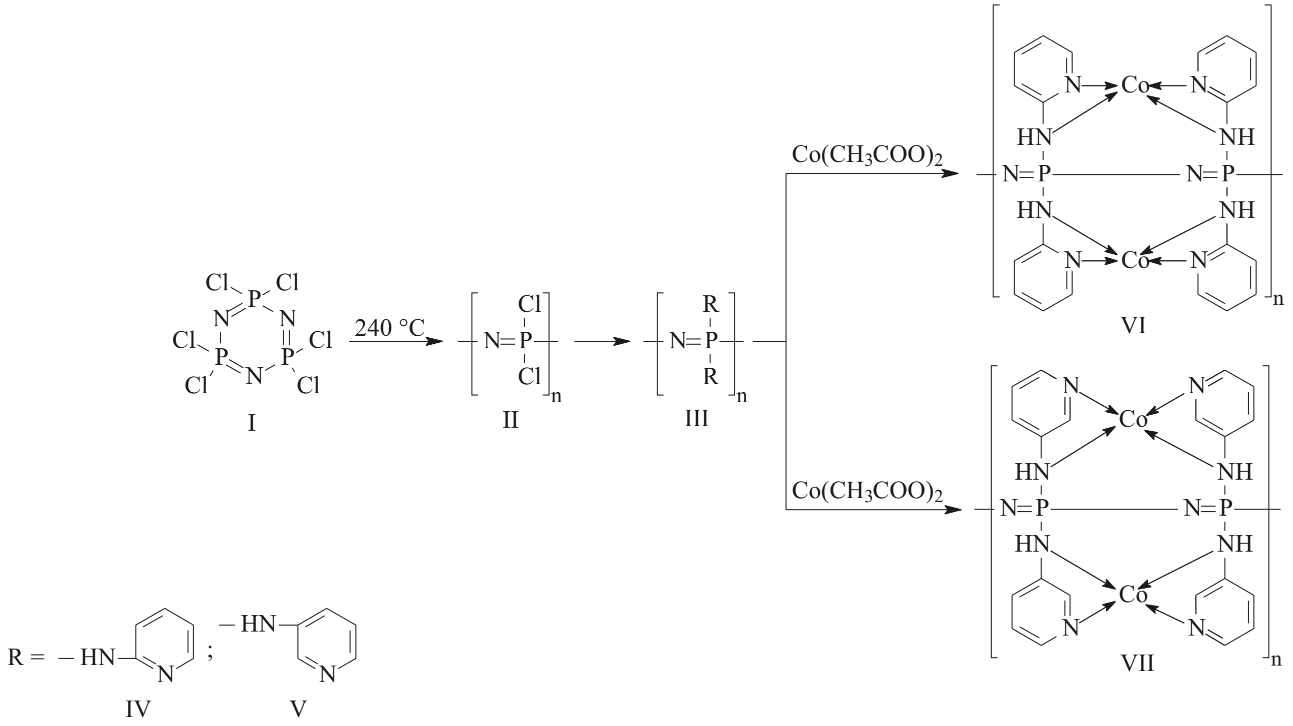
— **Polymerization of phosphonitrilic chloride trimer, at 240 °C during 24 h**. The method is based on the ring-opening polymerization of the heterocyclic trimer (I). Hexachlorotriphosphazene (2 g) was placed in a sealed ampoule and heated in a furnace at 240 °C until the clear melting mixture became highly viscous but still slightly mobile. The ampoule was opened and linear polymer $(NPCl_2)_n$ [formula (II)] was dissolved in dry toluene.

— **Substitution reaction, precipitation and purification of the crude product**. 2-Aminopyridine or 3-aminopyridine (0.017 mol), triethylamine (2.37 mL) were dissolved in 50 mL of dry THF. Next 1 g poly(dichlorophosphazene) [formula (II)] dissolved in 10 mL of dry toluene and a small amount of catalyst — tetrabutylammonium bromide (TBAB) were added. The reaction mixture was refluxed for 48 h. The polymer [formula (III)] was isolated by precipitation in water. In both cases the reaction yield ranged from 80 to 90 %.

— **Preparation of cobalt complexes of poly(diaminopyridinophosphazenes)**. Into 50 mL of acetonitrile poly(diaminopyridino)phosphazene (0.5 g) and cobalt acetate(II) (1 g) were added. The mixture was stirred for 48 h at room temperature. Next, the catalyst were filtered from the reaction mixture and washed several times with acetonitrile. The catalyst was dried and kept in exsiccator.

It in this way two complexes which were catalysts were received:

— poly[bis(2-aminopyridine)phosphazene] + cobalt acetate (catalyst 1),

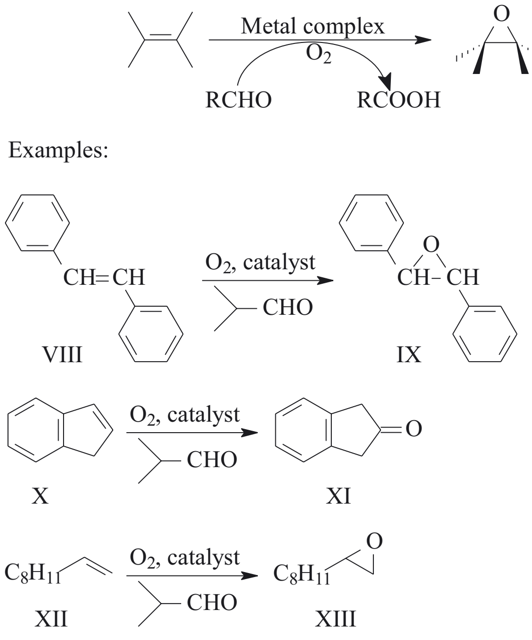


Scheme A. Preparation of catalysts by polymerization and substitution reactions

— poly[bis(3-aminopyridine)phosphazene] + cobalt acetate (catalyst 2).

Oxidation reactions

The oxidation reactions were carried out in thermostatic reactor at 60 °C at atmospheric pressure in the presence of oxygen. The 2-methylpropanal was used as a reductant and co-catalyst [13, 14]. 5 mmols of substrates such as *trans*-stilbene, indene, 1-decene [formulas (VIII), (X) and (XII), respectively] were dissolved in 20 mL of acetonitrile and then 10 mmols of isobutyl aldehyde and 20 mg of catalyst were added to the mixture. The reaction progress was controlled by the gas chromatography (GC-MS). Finally, the organic layer was dried and the solvent was evaporated to give the product required. All products were characterized by analytical and spectroscopic data.



Scheme B. Oxidation of alkenes

The oxidation reaction is showed in Scheme B.

Method of testing

The products were analyzed by IR spectroscopy (KBr technique, range from 400 cm^{-1} to 4000 cm^{-1}) using BIO RAD FTS 165.

Thermogravimetric analysis (TG) was performed using a Netzsch TG 209. For all the tests the sample weight was ~4 mg and measurements were performed in argon atmosphere at temperature from 30 °C to 600 °C with heating rate 10 K/min.

Atomic absorption spectrometry (AAS) measurements were done using apparatus Perkin Elmer Analyst 300. The samples of catalysts were demineralized in 65 % nitric acid and submitted the ionization reaction using the oxyacetylene blowpipe. Next, the sample were analyzed using the standard cobaltic cathode. The oxidation reactions were controlled by GC-MS [Hewlett- -Packard Gas Chromatograph 5890 Series II using Hewlett-Packard Ultra 1 column (30 m × 0.25 mm × 0.25 μm), in a quadrupole mass analyzer; carrier gas — helium].

RESULTS AND DISCUSSION

Poly(diaminopyridinophosphazene) was analysed by IR spectroscopy.

The structure of poly[bis(2-aminopyridine)phosphazene] was confirmed by the presence of the following bands (cm^{-1}): 3380 ($\nu_{N\text{-}H}$), 1600 (ν_{CN}), 1480 ($\nu_{C_5H_4N}$), 1280 ($\nu_{P\text{-}N\text{-}Ph}$), 770 ($\nu_{P\text{-}N\text{-}P}$). Similar bands was observed for poly[bis(3-aminopyridine)phosphazene]: 3430 ($\nu_{N\text{-}H}$), 1630 (ν_{CN}), 1500 ($\nu_{C_5H_4N}$), 1250 ($\nu_{P\text{-}N\text{-}Ph}$), 750 ($\nu_{P\text{-}N\text{-}P}$).

The complexes were characterized by AAS and TG methods. The AAS measurements show that the cobalt content is 54.9 mg/1 g sample for catalyst 1 and slight higher *i.e.* 55.7 mg/1 g sample for catalyst 2.

Table 1. Results of TG analyses of catalysts

	$T_{1\%}$ °C	$T_{3\%}$ °C	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{20\%}$ °C	$T_{30\%}$ °C	$T_{50\%}$ °C	Stable residue %
Catalyst 1	53.5	75.5	94.5	140.5	255.5	304.5	382.5	56.0
Catalyst 2	50.9	72.9	104.9	186.9	261.9	309.9	349.9	45.9

The thermal properties of the catalyst were investigated by TG method. The findings are shown in Table 1 and Fig. 1. Both catalysts have similar thermal proper-

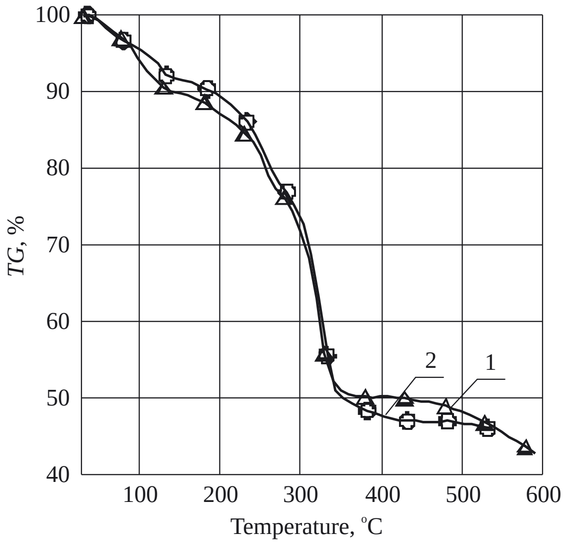


Fig. 1. TG profiles of catalysts: 1 — catalyst 1, 2 — catalyst 2

ties. Both complexes decomposed properly in two steps. The first step, mass loss of about 10 % for catalyst 1 and 2 was at 140.5 and 186.9 °C, respectively, and mass loss of about 50 % for catalyst 1 was at 382.5 °C and 349.9 °C for catalyst 2. Whereby, the amount of solid residue was 56.0 and 45.9 %, respectively (Table 1, Fig. 1). It was shown that the catalyst 2 was more stable in the first step while catalyst 1 was more stable in the second step. Decomposition at $T_{10\,\%}$ for both catalysts results probably from cleavage of bond coordinated with metal, however mass loss at $T_{50\,\%}$ was caused by decomposition of a polymer.

Table 2. Results of oxidation reactions

Catalyst	Substrate					
	trans-stilbene		indene		1-decene	
	yield, %	time, h	yield, %	time, h	yield, %	time, h
Catalyst 1	67	3	90	1	33	30
Catalyst 2	80	1	92	1	37	30

The results of oxidation reactions are listed in Table 2. In our reactions, *trans*-stilbene [formula (VIII) in scheme B] gives epoxide [formula (IX) in Scheme B] and indene [formula (X) in Scheme B] gives ketone [formula (XI) in Scheme B] with very high selectivity and relatively high yield. The oxidation reaction of indene needs shorter time than oxidation of *trans*-stilbene. The best results were obtained for poly[bis(3-aminopyridine)phosphazene] + cobalt acetate.

Alkenes with terminal double bond show low reactivity therefore they need longer reaction times. Under these conditions 1-decene [formula (XII) in Scheme B], gives epoxide [formula (XIII) in Scheme B] 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 double bond is activated by the presence of another group. In comparison, the investigations described in literature [15] on polymers-supported manganese porphyrin gave similar results in oxidation reactions, but they needed longer reaction time.

CONCLUSIONS

The polyphosphazene-based catalysts are very effective in oxidizing of alkenes under mild conditions. The main advantage of these catalysts are their efficiency, selectivity and simplicity of separation of 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 oxidation catalysts, but further physical and chemical research works should be conducted.

REFERENCES

1. Hirao T., Higuchi M., Ohshiro Y., Ikeda L: *J. Chem. Soc., Chem. Comm.* 1993, **2**, 194.
2. Hirao T., Higuchi M., Hatano B., Ikeda L.: *Tetrahedron Lett.* 1995, **36**, 5925.
3. Higuchi M., Imoda D., Hirao T.: *Macromolecules* 1996, **29**, 8277.
4. Wentzel B., Leinonen S., Thompson S., Sherrington D., Feiters M., Nolte R.: *Perkin Trans.* 2000, **1**, 3428.
5. Pol. Appl. PL 323 292 (1997).
6. Bhaskar C., Iqbal J.: *Tetrahedron Lett.* 1997, **38**, 1235.
7. Kowalski G., Pielichowski J.: *Synlett* 2002, **12**, 2107.
8. Cao Y., Andreatta A., Heeger J., Smith P.: *Polymer* 1989, **30**, 2305.
9. Allcock H. R.: *Inorg. Macromol., Chem. Eng. News* 1985, **63**, 22.
10. Allcock H. R.: *Polym. Mater. Sci. Eng.* 1997, **49**, 76.
11. Burczyk A., Pielichowski J., Bogdał D.: *Pol. J. Chem. Technol.* 2003, **5**, 96.
12. Burczyk A., Pielichowski J.: *Polimery* 2004, **49**, 486.
13. Burczyk A., Bogdał D., Pielichowski J.: *Przem. Chem.* 2003, **10**, 1370.
14. Burczyk A., Pielichowski J.: *Modern Polym. Mater. Envir. Appl.* 2004, **1**, 29.
15. Moghadama M., Tangestaninejad S., Habibi M., Mirkhani V.: *J. Mol. Catal.* 2004, **217**, 9.

Received 11 VII 2005.
Revised 14 X 2005.