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New Catalysts Based on Poly(aspartic acid) for Oxidation Reaction

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In the current work we describe synthesis of novel poly(D, L-aspartic acid) catalysts for oxidation reactions. The catalysts were prepared by a three-step reaction procedure. First, poly(D, L-aspartic acid) (PAA) was synthesized by polycondensation reaction D, L-aspartic acid with propylene carbonate under microwave irradiation. In the second stage, poly(aspartic acid) sodium salt (PAA-Na) was obtained during the reaction of hydrolysis of cyclic forms of PAA in water solutions of sodium. The last stage of catalysts synthesis were reaction of poly(aspartic acid) sodium salt with cobalt or copper acetate. FTIR, ^{1}H NMR, SEM, SEM-EDS, and SIMS were employed for characterization of the obtained catalysts were employed for characterization of the obtained catalysts. Oxidation reactions of some compounds were carried out on synthesized catalysts at atmospheric pressure in the presence of molecular oxygen. As the main products epoxides and ketone were obtained with very high yield and selectivity.

Keywords Alkenes; oxidation reactions; poly(aspartic acid); polymer catalysts

Introduction

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 the Mukaiyama procedure, where substrate is epoxidized using a transition metal complex as catalyst, molecular oxygen as oxidant and an aliphatic aldehyde as co-reactant. Transition metal complexes, such as Schiff's base complex, are also suitable for the aerobic epoxidation of alkenes with a co-reacing aldehyde. For example, cobalt(II) Schiff's bases give good results; however, these catalysts are rather not selective for epoxidation.

It has been reported in 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. As an example, a polyaniline-supported cobalt(II) catalysts were prepared first by Pielichowski and Iqbal and used for the aerobic epoxidation of alkenes.

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For example, a polyaniline-supported catalyst has been used for epoxidation of *trans*-stilbene with very high yield and selectivity [1–5].

In the last decade biodegradable polymers have deserved a special attention as their decomposition products are non-toxic. To this group of polymers – due to its advantages – belongs e.g., poly(aspartic acid) (here: PAA), which is a biologically inert polyamino acid. Poly(aspartic acid) has been recently very intensely examined over the possibility of the utilization of PAA and its derivatives in medicine and agriculture [6–8]. Because poly(D, L-aspartic acid) have functional groups to coordinate, thus, in this paper, we report on novel poly(aspartic acid) supported cobalt(II) or copper(II) catalysts, which were tested in the oxidation processes of hydrocarbons – it is hoped that the catalysts chemically linked with polymeric support will be stable and able to be separated easily after the reaction.

These catalysts, based on poly(aspartic acid), have been obtained and tested in *trans*-stilbene, indene and 1-decene oxidation reactions.

Experimental

In the Department of Chemistry and Technology of Polymers, Cracow University of Technology has used new, original method synthesis of poly(aspartic acid) under microwave irradiation. The application of the microwave irradiation has permitted shortening of polymerisation time to several minutes, increase in efficiency and elimination of the catalyst – this fact is very important in synthesis compounds, which are used for the preparation of catalysts.

The general method for poly(aspartic acid) sodium salt (PAA-Na) synthesis is illustrated in Figure 1.

In our experiments the catalyst were prepared by a three-step method:

(1) Polycondensation of aspartic acid
The synthesis of cyclic PAA was carried out in a microwave reactor "Milestone" of 1000 W capacity. Polycondensation of cyclic PAA was realized at the temperature range from 176°C to 230°C, carbonate propylene was used as solution. Water was removed from the system by an azeotropic distillation under normal pressure. Cyclic PAA was precipitated with methanol, washed in water and dried. The reaction efficiency was above 93%.

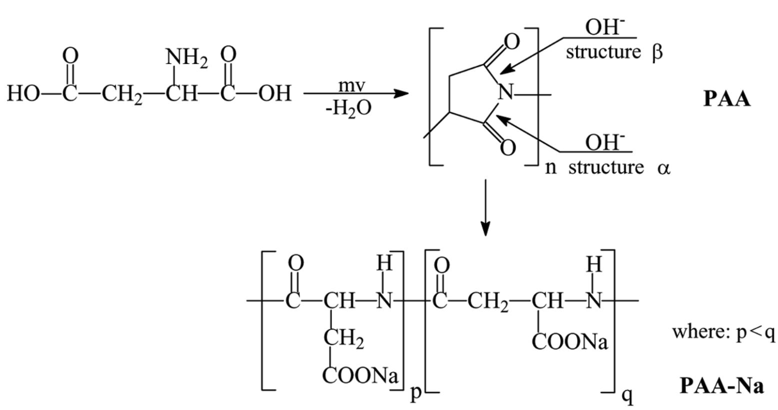


Figure 1. Synthesis of PAA sodium salt.

(2) Hydrolysis of cyclic forms of PAA

PAA sodium salt has been obtained during the reaction of hydrolysis of cyclic forms of PAA, water solutions of sodium. The process of hydrolysis was carried out in the solution with pH = 8.5 to 13.0 [4].

The obtained product was identified by FT-IR and ^{1}H NMR:

FT-IR (KBr): characteristic absorption band of stretching vibrations of C=O group is about 1610 and 1660 cm^{-1}, strong absorption band of OH stretching vibrations is in the range of 3400–3500 cm^{-1}

^{1}HNMR (D_2O): the methane proton is seen as two resonances at about 4.7 and 4.5 ppm, the methylene protons are observed as three resonances at about 2.8, 2.7 and 2.55 ppm.

(3) Synthesis of complex of PAA sodium salt with cobalt(II) or copper(II) acetate

The complex of PAA sodium salt with cobalt(II) or copper(II) acetate was obtained by mixing of 1.00 g of PAA-Na with the corresponding amount of metal acetate.

In this way were obtained two catalysts:

– PAA-Na + cobalt acetate – **PAA-Co**
– PAA-Na + copper acetate – **PAA-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 the 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.

Trans-stilbene, 1-decene and indene were subjected to the oxidation reactions.

Results and Discussion

The two catalysts – PAA-Co and PAA-Cu – were examined by SEM/EDXS. 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 to map the surface topography and compositional contrast based on the density differences. The X-rays emitted when the electron beam struck 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. Prior to the analysis the catalyst samples were coated with conductive carbon films to a thickness of 20–30 nm. The surface images of the catalysts are shown in Figure 2. It can be seen that these heterogeneous catalysts created agglomerates with the size of the order of 20–40 μm and smaller, of

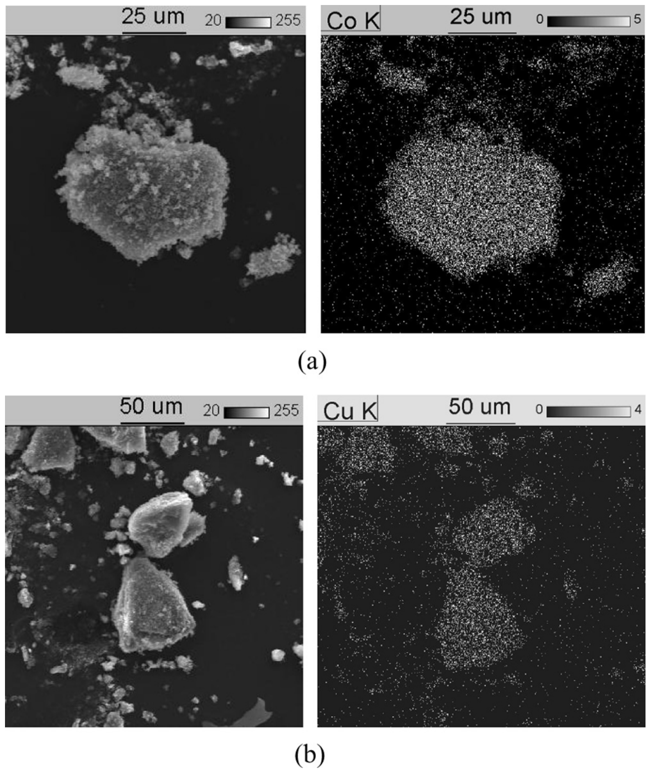


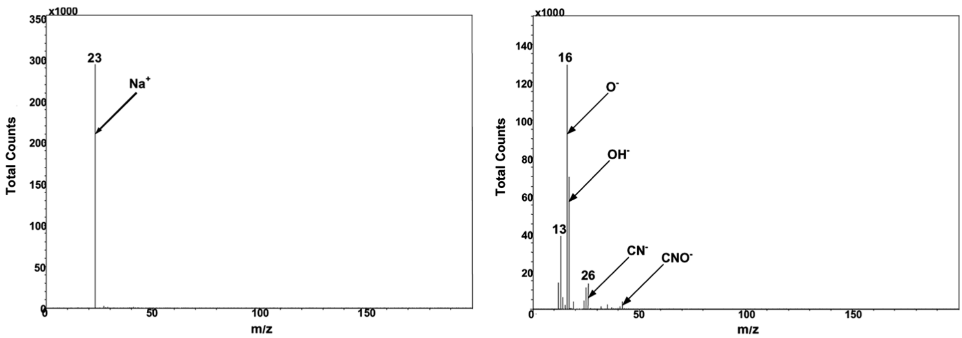
Figure 2. SEM images of (a) PAA-Co, (b) PAA-Cu and metals distribution on PAA cobalt (a) and copper (b) respectively.

about 5–10 μm. These agglomerates consist of many smaller spherical grains in case of PAA-Co and flaky-lamellar ones for PAA-Cu.

The application of EDS spectroscopy coupled with SEM let us test the surface distribution of chemical elements, for example metals, in the form of a surface map – Figure 2. We observed that metal was spaced exactly on the catalyst surface. We can suggest that a chemical reaction took place between the polymer and cobalt or copper(II) salt, and only one compound was obtained.

The received catalysts were tested for the presence of metals using time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS measurements were performed using a PHI TRIFT 2100 time-of-flight secondary ion mass spectrometer equipped with gallium liquid metal ion gun (LMIG). This instrument allows spectroscopy, for the characterization of surface chemical composition. The system uses a pulsed primary ion beam to desorbs and ionize species from a sample surface [9–13].

The results for PAA-Na and its cobalt and copper derivatives, assigned as PAA-Co and PAA-Cu respectively, are reported here. Positive mass spectrum of PAA-Na is dominated by sodium (Fig. 3), which reflects low ionization potential of this metal under the measurement conditions. The secondary fragment ions, despite their low intensities, support the structure of PAA-Na. The characteristic fragments of PAA-Na ions present in positive and negative mass spectra are shown



(a) (b)

Figure 3. Positive secondary ion mass spectrum (a) and negative secondary ion mass spectrum (b) of PAA-Na.

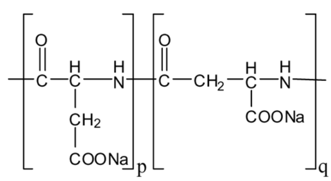
in Table 1. The lines are of low intensities and 93% of the total positive ion emission originates from sodium.

The process of ion exchange resulted in the replacement of mobile sodium ions with cobalt ion, which is shown in Figure 4. The spectra clearly indicate that most of the sodium was substituted during the process. The spectrum for PAA-Cu is similar for PAA-Co.

Figure 4 show the presence of the $[COCo]^+$ fragment, which suggests incorporation of cobalt into the precursor's structure (not just a copper oxide).

The characteristic fragments of PAA-Co and PAA-Cu ions present in positive mass spectra are shown in Table 2.

Table 1. Characteristic fragments of PAA-Na ions present in positive and negative mass spectra



Characteristic Fragments of Ions

Positive		Negative	
Formula	m/z, amu	Formula	m/z, amu
$[CH_2N]^+$	28.02	$[CN]^-$	26.00
$[CH_4N]^+$	30.03	$[CNO]^-$	42.00
$[CONH_2]^+$	44.01	$[COOH]^-$	45.00
$[C_2H_6N]^+$	44.05	$[C_3H_3O]^-$	55.03
$[CH_2O_2]^+$	46.01	$[C_2H_2O_2]^-$	58.01
		$[C_3H_3O_2]^-$	71.01
		$[C_2H_2NO_2]^-$	72.03

Table 2. Characteristic fragments of ions present in positive mass spectra of PAA-Co (cobalt modification) and PAA-Cu (copper modification)

PAA-Co		PAA-Cu	
Formula	m/z, amu	Formula	m/z, amu
Co^+	58.93	Cu^+	62.93
$[CoO]^+$	74.93	$[CuO]^+$	78.92
$[CoOH]^+$	75.94	$[CuOH]^+$	79.93
$[CoOH_2]^+$	76.95	$[CuOH_2]^+$	80.94
$[COCo]^+$	86.92	$[COCu]^+$	90.92
$[CHOCo]^+$	87.93	$[CHOCu]^+$	91.93
$[CH_2OCo]^+$	88.94	$[CH_2OCu]^+$	92.94

The presence of $[COCo]^+$ and $[COCu]^+$ fragment ions provides evidence for the chemical interaction between the catalyst precursor (PAA-Na) and both the cobalt and copper cations. It means that these metals are not simply supported as their oxides on PAA-Na but they are chemically incorporated into it.

Catalytic Oxidation

Using these catalysts the aerobic oxidations of different organic compounds – *trans*-stilbene, 1-decene and indene – have been carried out. The results of catalytic oxidation of organic compounds are collected in Table 3. Selectivity of the main products was given and the reaction time was shown in brackets.

Trans-stilbene and 1-decene give epoxides, but indene gives ketone (1,3-dihydro-2H-inden-2-on) with very high selectivity. The oxidation reaction of 1-decene needs longer time than the oxidation of *trans*-stilbene and indene. Under these conditions 1-decene gives epoxide with very high selectivity. No changes in yield were observed when the same reactions were carried out longer. The 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 [14].

Table 3. Results of the polymer – supported cobalt and copper catalysts oxidation with molecular oxygen

	Products Selectivity [%] (time [h])		
Catalysts	Epoxystilbene	Epoxydecene	Indene-2-one
PAA-Co	85 (0.5)	62 (30)	98 (1)
PAA-Cu	91 (0.5)	56 (32)	97 (1)

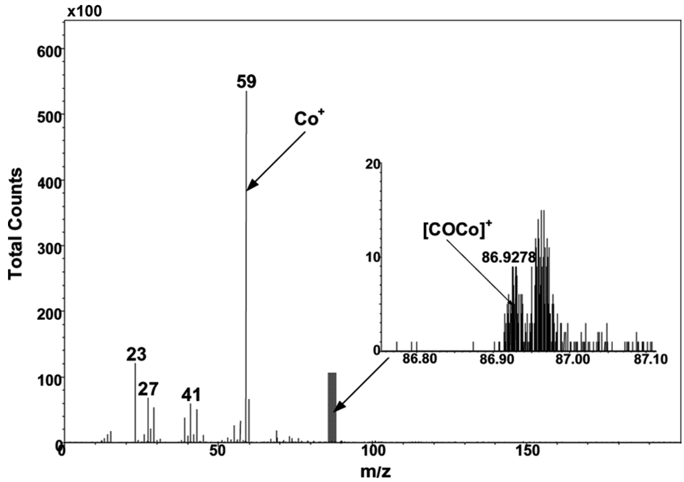


Figure 4. Positive secondary ion mass spectrum of PAA-Co.

Conclusion

In conclusion, we have described the synthesis of poly(aspartic acid) – 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 a relatively short time. Generally, poly(aspartic acid) can be considered as a new group of macromolecular oxidation catalysts, with advantageous properties.

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