CATALYTIC ACTIVITY OF POLYMER-SUPPORTED COBALT(II) CATALYSTS IN THE OXIDATION OF ALKENES

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Abstract

The oxidation of organic compounds with carbon-carbon double bond using of molecular oxygen under atmospheric pressure in the presence of new polyaniline supported catalyst has been studied.
Oxidation reactions were carried out in relatively mild conditions in presence of molecular oxygen under atmospheric pressure at temperature 333K. Alkenes with terminal carbon-carbon double bonds were selectively oxidized to corresponding epoxides with very high yield and selectivity. Cyclic alkenes were easily oxidized mainly to epoxides. Oxidation of hydrocarbons in benzyl position gives ketones as main products.

Keywords:

polymer supported catalysts, polyaniline, hydrocarbons oxidation

Introduction

A new family of materials destined to solve many different technical and ecological problems – conducting polymers known as the organic metals – is in development. Polymer supported metal complexes are gaining importance as efficient heterogeneous catalysts in a variety of organic transformations including oxidation, which constitute an important group of processes both in laboratory and industrial scale. However, the toxicity of some widely used oxidants and the need for a solvent are the main obstacles in the further development. Many oxidation processes are characterized by low selectivity, which makes them much more difficult in application [1–6]. From environmental as well as economic point of view catalytic oxidation processes, especially those with molecular oxygen used as primary oxidant are particularly attractive. The use of polymer supported catalysts offers several additional benefits in preparative procedures. The main advantage of this type of catalysts is much simpler products purification, the possibility of isolation of a catalyst as well as reuse of catalyst and enhanced stability [7,8]. Heterogeneous catalysis allows running of various processes in a selective way and under mild conditions.

It has been reported in the literature that oxidation of organic compounds by various oxidants can proceed efficiently when a polymer-supported catalyst is used. A polymer is typically very stable even in an oxidative atmosphere. Polyaniline (PANI) is one of the polymers which can be employed as a catalyst support used in oxidation of a wide range of organic compounds [9,10]. It is cheap, easy to synthesize and insoluble in commonly used solvents. Moreover, its unique electronic properties are related to its π-conjugated structure. Doping reaction modifies the electronic properties of those polymers and therefore they are able to transport electrons. Protonic acid doping converts a semiconducting emeraldine base to the conductive derivative. Our previous papers demonstrated that polyaniline (PANI) supported with cobalt or cobalt complexes serve as a synthetic metal catalyst in the oxidation of different varieties of alkenes [11–13]. Coordination of transition metal atom to the nitrogen permits transition metals to interact with each other through the π-conjugated chain of the polymer. The complexation of PANI with cobalt(II) acetate, cobalt(II) chloride or cobalt(II) Salen complex was found to form more efficient synthetic metal catalytic system in epoxidation reactions. Polyaniline supported catalysts based on cobalt(II) salts and its complexes were prepared first by J. Pielichowski and J. Iqbal and used for epoxidation of some alkenes [14–17].

In this paper, we report a specific series of oxidation reactions of unsaturated organic compounds with using polyaniline supported cobalt(II) catalysts. Our aim was to combine the advantages of supported catalysts and inexpensive oxidant – molecular oxygen.

Experimental

2.1. Materials

Aniline (POCh) reagent grade was distilled under reduced pressure in the presence of zinc powder. Acetic acid and acetonitrile Merck products were used as solvents without further purification. Cobalt chloride and cobalt acetate were obtained from POCh Gliwice, whilst all other chemicals were reagent grade, purchased from Sigma-Aldrich and used without any further purification.

2.2. Preparation of Polyaniline (PANI)

In a typical procedure, freshly distilled aniline (107 mmol, 10 g) was dissolved in 120 ml of 1.5 M HCl aqueous solution. The solution was then cooled to 268 K in an ice-salt mixture. After that water solution of ammonium persulfate (134 mmol, 30.5 g) was added dropwise to the vigorously stirred solution. Taking into account exothermic nature of polymerization reaction, rate of addition of oxidizing agent was controlled by the temperature of the reaction mixture. The temperature should be between 268–270 K. After adding of ammonium persulfate the solution was stirred for 4 h. The greenish black precipitate was filtered off and washed with distilled water until the filtrate became colorless. Oligomers were extracted from polyaniline with methanol and then with tetrahydrofuran in a Soxhlet apparatus until the solvent became colorless. The polymer was then dried at 333 K for 24 h and deprotonated with 250 ml of 12% aqueous ammonia solution by mixing in room temperature for 6 h. Deprotonated polymer was filtered off and washed with water until filtrate became colorless, after that it was dried at 333 K for 24 h. Purification steps are very important for the complete removal of all oligomeric species.

2.3. Polymer-supported Cobalt(II) Acetate and Cobalt(II) Chloride

Presented procedure of cobalt(II) salts immobilization was used in PANI doping with cobalt chloride and cobalt acetate.

A mixture of polymer (500 mg) and cobalt acetate (500 mg) was stirred in acetonitrile (25 ml) and acetic acid (25 ml) at room temperature for 72 h. After that, the reaction mixture was filtered and the solid catalyst was washed with acetonitrile (5 x 5 ml). The catalyst was dried at 383 K for 24 h.

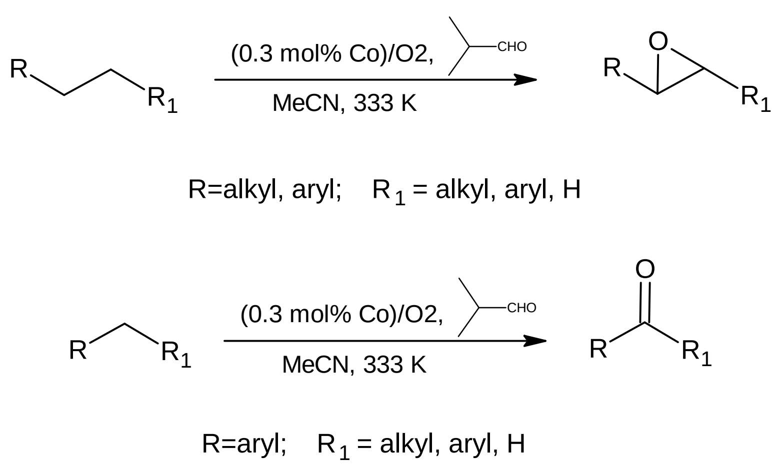
2.4. General Procedure for Organic Compounds Oxidation.

The Oxidation of dec-1-ene is Representative for the General Procedure Employed for the Oxidation

The mixture of 2-methylpropanal (1.08 g, 15mmol) and polymer-supported catalyst (30 mg) was dissolved in MeCN (30 ml). The mixture was bubbled with oxygen for 15 min at 333 K. Then, dec-1-ene (0.7 g, 5 mmol) was added. The reaction was carried out under oxygen atmosphere for the time period indicated in Table 1. After completion of the reaction the catalyst was filtered and the solvent was evaporated to yield a residue, which was dissolved in ethyl acetate and washed with $NaHCO_3$ solution and water. The organic phase was dried over $MgSO_4$ and the evaporation of solvent yielded the desired product, which was purified by Kugelrohr distillation.

Results and Discussion

We have recently reported that cobalt(II) salts and Salen complexes immobilized in polyaniline (PANI) matrix catalyze the oxidation of different organic compounds in mild conditions (Scheme 1). Reactions were carried out in the presence of molecular oxygen under atmospheric pressure at 333 K.

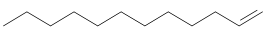
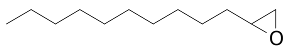
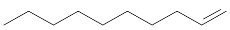
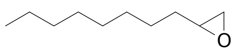
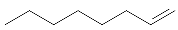
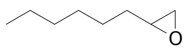
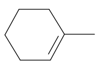
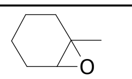
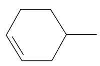
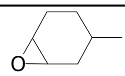
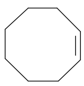
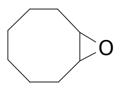
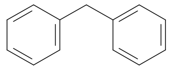
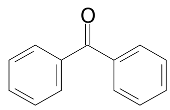
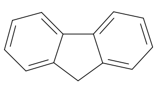
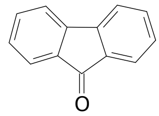
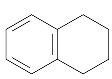
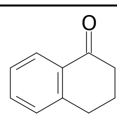


Scheme 1. Hydrocarbons oxidation with $CoCl_2$ and $Co(CH_3COO)_2$ immobilized in polyaniline matrix.

Moreover more detailed comparison of catalysts was carried out in testing oxidation reaction of dec-1-ene. Two different catalytic systems were tested. Cobalt(II) chloride **1** and cobalt(II) acetate **2** immobilized on polyaniline matrix were used. In our previous investigation on the oxidation of organic compounds we have found that polyaniline supported with cobalt(II) salts or complexes are recyclable and catalyze efficiently the oxidation of alkenes to corresponding epoxides [11–13].

The oxidation reaction results given in Table 1 (entry 1-3) indicate that alkenes with terminal carbon-carbon double bonds could be selectively oxidized to corresponding epoxides with very high yield. The epoxides were the sole products, the presence of by-products was not observed. Oxidation of cyclic alkenes is much easier, taking into account that C=C bonds are much more reactive than in alkenes with terminal double bond. The alkenes formed corresponding epoxides within 1-8h depending on substrate used (Table 1, entry 4-6). Oxidation of 4-methyl-1-cyclohexane leads to corresponding monoepoxide with 100 % yield after 4 h of reaction. Its isomer 1-methyl-1-cyclohexane reacts so rapidly that substrate is consumed completely after 30 min of reaction. Gas chromatography showed that initially epoxy derivative is formed as intermediate product and then in reaction conditions degradation occurs to products of epoxide decomposition. 1-Cyclooctene required a slightly longer reaction time compared to methylcyclohexenes to afford corresponding epoxide as sole product in 92 % yields. It was also observed that catalyst with cobalt(II) chloride **1** is slightly more efficient than that based on cobalt(II) acetate **2**.

Table 1. Results of the polymer-supported cobalt catalysts oxidation of hydrocarbons with molecular oxygen[a]

Entry	Substrate	Catalyst	Time, h	Yield, %	Product
1		**1**	24	86	
		2		83	
2		**1**	24	89	
		2		90	
3		**1**	18	99	
		2		99	
4		**1**	0,5	–[b]	
		2		–[b]	
5		**1**	4	100	
		2		100	
6		**1**	8	92	
		2		87	
7		**1**	24	85	
		2		83	
8		**1**	24	92	
		2		91	
9		**1**	24	45	
		2		45	

[a] Substrate (5 mmol) and catalyst **1** or **2** (30 mg, 0.3 mol % equiv. Co) were stirred at 333 K under oxygen atmosphere for the appropriate time.
[b] Complete conversion of substrates; decomposition of products in reaction conditions.

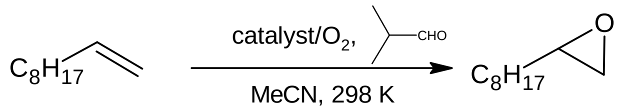
Oxidation of hydrocarbons in benzyl position is much more efficient in comparison to oxidation of alkenes due to the possibility of forming resonance trapping radicals or benzyl cations. Catalytic activity of our catalysts were tested in oxidation of a series of organic compounds diphenylmethane (entry 7), fluorene (entry 8) and 1,2,3,4-tetrahydronaphthalene (entry 9). Reactions were carried out in identical conditions to that for previous compounds. Ketones were formed as the main products with high yield and selectivity. There were some differences in yields in diverse reactions. This phenomenon could be explained by stabilizing of radicals formed as intermediate products, by the presence of two aromatic rings in their vicinity. The best results were observed in oxidation of diphenylmethane (yield 83–85 % to acetophenone) and fluorene (yield 91–92 % after 24 h, 9*H*-fluorene-9-one is formed). Oxidation of and 1,2,3,4-tetrahydronaphthalene (entry 9) is less efficient due to the fact that radicals are stabilized with only one aromatic ring. It could be assumed that the results for both catalysts are comparable.

Due to the fact that the amount of cobalt salt immobilized on polyaniline support is a critical factor in the oxidation, a more detailed comparison of catalysts was carried out in testing reaction of dec-1-ene oxidation (Scheme 2). Two different catalytic systems were tested – cobalt(II) chloride **1** and cobalt(II) acetate **2**, both immobilized on polyaniline matrix. In the polymer doping reaction different ratios of cobalt(II) salts and polyaniline were used as it was presented in Table 2. Summarized results of Co(II) content in different catalysts show that cobalt content has been increasing when different amounts of cobalt(II) acetate were used in doping reaction (samples 2A-2D), whereas when cobalt(II) chloride was used there was no significant changes in total Co(II) content (samples 1B-1E). It was observed that the amount of Co(II) immobilized on PANI was increasing to reach about 30 mg of Co(II) per gram of sample, after that some kind of saturation of PANI surface was observed and no further changes was observed even when the amount of $CoCl_2$ used in the doping reaction was increasing. It determined further research of whether Co(II) concentration measured with atomic absorption spectroscopy corresponds to catalytic activity of catalyst or some part of cobalt present in polyaniline matrix could be inactive in oxidation reactions.

Table 2. Total content of Co(II) in catalysts depending on catalyst: PANI weight ratio used in doping reaction.

Catalyst	Co(II) Source	Catalyst/ PANI wt ratio, g/g	Co(II) content*, mg_{Co}/g_{sample}
1A	$CoCl_2$	1 : 2	11.2
1B		1 : 1	30.0
1C		2 : 1	30.4
1D		4 : 1	31.0
1E		10 : 1	34.6
2A	$Co(CH_3COO)_2 \cdot 4H_2O$	1 : 4	14.1
2B		1 : 2	13.4
2C		1 : 1	16.9
2D		2 : 1	25.1

*Co(II) content after doping reaction was determined with using of AAS method



Scheme 2. Dec-1-ene oxidation with **1A**-**1E** and **2A**-**2D** catalysts with molecular oxygen

Oxidation reactions of dec-1-ene were carried out in acetonitrile at 298 K in the presence of aldehyde with molecular oxygen at atmospheric pressure. Only one product was observed – 2-octyloxirane. The reaction progress was monitored with GC equipped with flame ionization detector. The results of these reactions are summarized in Figs. 1 and 2. In addition, for comparative purposes of oxidation activity of homogeneous and heterogeneous catalysts, the reaction was conducted with the use of $CoCl_2$ and $Co(CH_3COO)_2$ without a polymer matrix. T. Hirao [18,19] studies show that PANI can be oxygen carrier in the oxidation reactions. It determined our further research on the possibility of catalyzing of oxidation reaction with the use of polyaniline without cobalt compounds immobilized on its surface. It was found that PANI shows no catalytic activity in the oxidation of dec-1-ene.

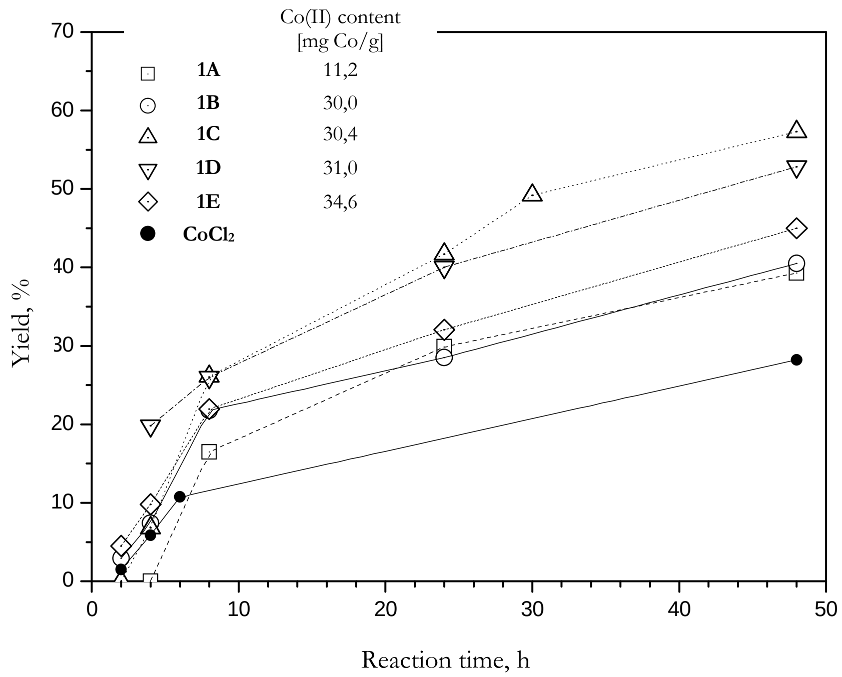


Fig. 1. Dec-1-ene oxidation on PANI immobilized with $CoCl_2$ at 298 K (**1A-1E**)

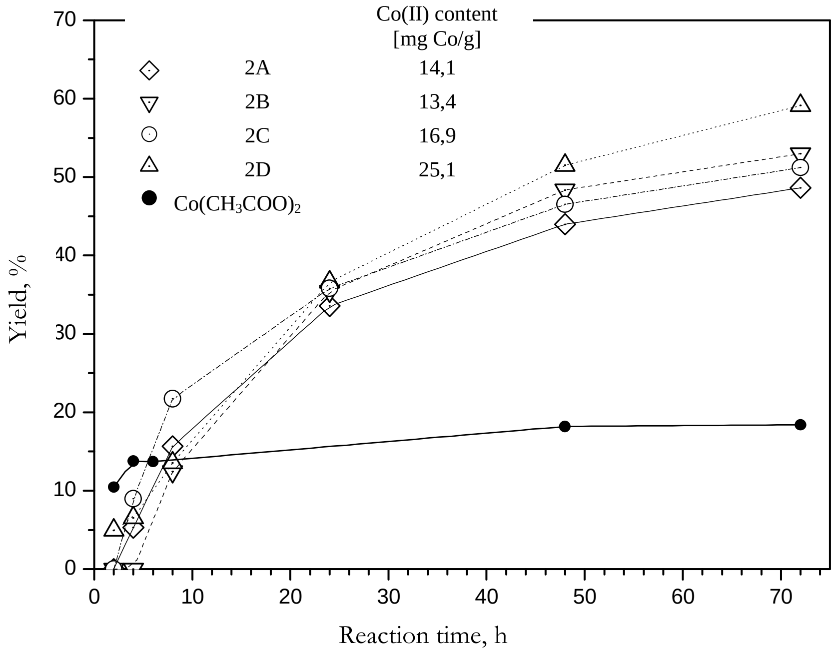


Fig. 2. Dec-1-ene oxidation on PANI immobilized with $Co(CH_3COO)_2$ at 298 K (**2A-2D**)

In the case of PANI doped with $CoCl_2$ (Fig. 1) it was observed that at the beginning of the process (for 8 h), the reaction proceeds relatively quickly, and then the speed decreases, and finally after 48 h of the process the obtained yields are between 39 and 57 %. There were significant differences in the reaction yields. While the content of cobalt in catalysts **1B**-**1E** is relatively high and comparable (30.9–35.8 mg Co/g) but in the case of **1A** Co(II) the content is much lower – 11.3 mg Co/g. On the basis of these observations it can be concluded that there is no simple relation between the quantity of cobalt immobilized in PANI matrix and the yield of the oxidation process. It seems that the major impact may be caused by the structure of the polymer, which, depending on external conditions under which the process is carried out may change significantly. It can be assumed that a part of the cobalt catalytic centers is located inside the polymer clusters and is inaccessible for the reactants or is inactive in oxidation reactions.

Catalysts based on polyaniline doped with cobalt(II) acetate (Fig. 2, **2A**-**2D**) are characterized by significantly lower contents of Co (13.6–25.7 mg Co per g) than **1A**-**1E**, but their catalytic activity is higher in reference to the amount of Co(II) in immobilized in PANI matrix. In this group of catalysts yields increasing is observed when Co(II) content is higher. The reaction carried out using cobalt acetate (II) without polymer support runs with a much lower yield – 18 % of 2-octyloxirane after 72 h of reaction.

Conclusions

It may be concluded that the cobalt compounds immobilized on polyaniline are characterized by higher catalytic activity towards the oxidation of dec-1-ene then those where cobalt (II) compounds without polymer matrix is used. The yield of the oxidation reaction depends on cobalt compound which was used in PANI doping reaction. It seems that the method of the catalyst synthesis (atmosphere, mixing speed, the way of substrates addition, reaction time, temperature, *etc.*) has a significant influence on its structure and morphology and hence on the catalytic activity of the mentioned kinds of catalysts.

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