

Microwave assisted oxidation reaction on polyaniline containing heterogeneous catalysts.

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[Abstract](#) [Keywords](#) [Introduction](#) [Experimental](#) [Results and Discussion](#) [Literature](#)

ABSTRACT

The microwave assisted oxidation of anthracene on heterogeneous catalyst is presented. As the matrix for different heteropolyacids used as a catalyst for oxidation reaction with hydrogen peroxide and its adduct with urea the conducting polyaniline was chosen. All the microwave processes were compared to conventional reaction carried out in the same temperature conditions.

KEYWORDS

polyaniline, heterogeneous catalyst, oxidation, hydrogen peroxide, microwave assisted reactions.

INTRODUCTION

Among plenty of available synthetic macromolecules conducting polymers could be characterised by the growing interest as well in scientific and industrial application [1]. The phenomenon may be explained by its very interesting physiochemical properties. From the other hand, most of conducting polymers are completely insoluble in common solvents what dramatically limits its application; however, it can be useful when applying them as the catalyst bed [2]. One of the most known and detailed investigated conducting polymer is polyaniline (PANI), which can exist in many different oxidation states which conductivity strongly depends on protonation with organic or inorganic acids [3].

From the other hand application of microwaves in synthetic organic chemistry has already been shown in many publication [4]. The conclusions from the research, show that such kind of energy transport could have a big influence on both rate and selectivity of the reaction. The phenomenon seems to be a consequence of the interaction of microwaves with the matter by means of dielectric and conducting mechanism. In the accelerating of the reaction the inter phase polarization could also play an important role [5]. Because of conducting properties of PANI introduction of this polymer as a matrix of catalyst for microwave assisted reaction may give additional advantages for reaction system.

As a continuation of our earlier research on microwave assisted oxidation reactions [6] we now report the microwave oxidation of some aromatics (i.e. anthracene) using hydrogen peroxide and hydrogen peroxide urea adduct (UHP) as the oxidant and tungstosilic acid immobilised (by means of protonation) on polyaniline bed as the catalyst.

EXPERIMENTAL

*Catalyst synthesis*Type A

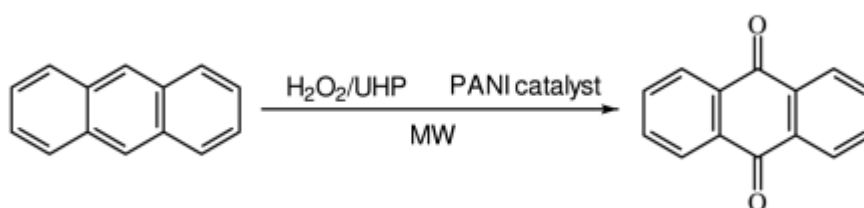
To the solution of aniline (21,5mmol, 1,96mL) in acetonitrile (90mL) the 12,5mmol of heteropolyacid was added. After the full homogenisation of the mixture the water solution of oxidant was added drop wised ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 26,7mmol, 6,08g). The addition of the oxidant was carried out at room temperature. After the oxidant addition was finished the system was left stirring for 24h. The obtained polymer was filtrated, washed with acetonitrile, water and methanol and finally dried and milled.

Type B

The catalyst synthesis was carried out in two steps: oxidative polymerisation of aniline and protonation of the polymer by heteropolyacid (dodecatungstosilic acid - HSiW or dodecatungstoboric acid HBW)

Polymerisation of aniline (prior distilled in vacuum) was carried out using classical oxidative polymerisation process conducted in the presence of potassium peroxodisulphate as the oxidant [7]. The reaction was set up below 4°C in the HCl water solution with the molar ratio aniline:oxidant 1:1.25. Aniline was dissolved in the acid solution, cooled down to 0°C. To this mixture the solution of oxidant in HCl was added drop wised according to the temperature which could not exceed 4°C. After the oxidant was added the mixture was stirred for 2 hours to complete the reaction. The precipitated polymer in its emeraldine form was washed with water and methanol. Polymer was deprotonated using 25% ammonia (24 hours), dried and in order to remove some oligomers the extraction with methanol was done.

Deprotonated polymer (1g) and 3g of heteropolyacid (HSiW or HBW) was intensively stirred at room temperature in the presence of 20mL of dry acetonitrile for 72h. After the process was finished the mixture was filtrated and catalyst was washed in acetonitrile, dried and milled.

Oxidation reaction

Scheme 1: Oxidation of anthracene on PANI catalyst.

According to the Scheme 1 all the reactions was carried out as follows. The substrate (1,5mmol) was dissolved in 20mL of acetonitrile and the catalyst was added to the solution. The amount of catalyst was calculated according to tungsten content in the sample estimated by AAS method. The concentration of tungsten was set up to the same level in all the reactions. Next 12mmol of H_2O_2 (1,2mL of 30% water solution) or urea hydrogen peroxide (UHP) was added to the mixture and it was heated conventionally or irradiated in microwave reactor (*Plazmatronika*, Poland, max. power 600W, applied power up to 35%) up to the boiling and than kept at reflux for time indicated in Table 1. After the reaction the

system was cooled and the catalyst was separated by filtration. The organic layer was evaporated and crude product was purified by means of preparative HPLC (methanol: water 80:20, detection UV at 254nm). The structure of the product was proofed by IR, HNMR and MS method.

RESULTS AND DISCUSSION

As a result of our investigation we have obtained a series of heterogeneous catalyst based on conducting polymer matrix, polyaniline. Because in the hydrogen peroxide oxidation protocols the most important factor is the amount of specific activator (tungsten atoms in this case) the detailed analysis of the presence of this element was carried out using EDS method (Table 1.). Going into details it is easy to observe that "one stage" method (A type catalyst) results in higher incorporation of the heteropolyacid into the matrix when compared to the protonation of polymer by the acid (B type catalyst). The phenomenon is observable for both applied acids, so it may be predicted that is independent from kind of the heteropolyacid. In the sample of catalyst recovered after the oxidation carried out in conventional conditions there is a quite high amount of tungsten lost from the matrix however the changes are much smaller in the type A catalyst what might guide to the conclusion that protonation method results in rather physical bounding of the heteropolyacid with the matrix. Such bounding type may be easy to destroy in during the oxidation process by simple washing out by the solvent.

Table 1. Tungsten content analysis of heterogeneous catalyst.

Catalyst	Tungsten content [%]
PANI/HSiW A	21.7
PANI/HSiW B	17.1
PANI/HBW A	25.3
PANI/HBW B	14.3
Catalyst recovered after the oxidation reaction (conventional conditions)	
PANI/HSiW A	15.9
PANI/HBW A	16.7
PANI/HSiW B	5.3
PANI/HBW B	4.2

The main goal of the presented investigation was to applying of synthesised catalyst in the microwave assisted oxidation using hydrogen peroxide and its urea adduct (UHP). All microwave experiments was compared to the conventional ones which has been conducted in the same temperature regime. The results of the oxidation processes i.e. the yield of 9, 10-antraquinodione are presented in Table 2.

Comparing the effectiveness of investigated catalytic systems it is easy to see that even when the amount of tungsten is equal the A type of the catalyst is presenting higher yield by means of the product of the oxidation reaction. In all cases the microwave assisted reaction may be characterised by the higher yield of the product obtained in the same periods of time. The situation is independent of the oxidant however the reactions applying UHP gives much smaller yields probably due to the long activation time understood as the dissociation of the adduct. Pure polyaniline does not affect as a catalyst at all when used in conventional conditions. From the other hand, traces of the product obtained in this catalytic system in

microwave conditions might testify about the catalytic effect caused by the interaction of conducting polymer with electromagnetic field at high frequencies

Table 2. Oxidation of anthracene at heterogeneous catalysts.

Catalyst	Oxidant	Time [min]	Yield [%]	
			MW	D
PANI	H ₂ O ₂	180	traces	0
	UHP		0	0
PANI/HBW A	H ₂ O ₂	120	59	27
	UHP		38	31
PANI/HBW B	H ₂ O ₂	180	17	7
	UHP		5	traces
PANI/HSiW A	H ₂ O ₂	120	48	31
	UHP		49	29
PANI/HSiW B	H ₂ O ₂	180	22	12
	UHP		9	5

As a conclusion we can say that presented study on microwave assisted oxidation reactions employing heterogeneous catalyst seems to be a new look on the role of microwaves interactions with the matter. It also proves our earlier investigation that hydrogen peroxide could serve as environmental friendly oxidant of many organic compounds which works effectively in microwave conditions.

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