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TWO-PHASE WACKER OXIDATION OF ALKENES CATALYZED BY WATER-SOLUBLE MACROMOLECULAR COMPLEXES OF PALLADIUM

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Abstract: New water-soluble macromolecular palladium complexes with phase transfer ability were used for two-phase Wacker oxidation of higher alkenes. Macromolecular metal complexes have been prepared employing as ligands monobutyl ether of polyethylene oxide and copolymers of ethylene oxide and propylene oxide functionalized by β,β'-iminodipropionitrile and acetodinitrile. Macromolecular metal complexes exhibited high activity and selectivity as catalysts for Wacker oxidation of different alkenes: octene-1, dodecene-1, hexadecene-1, styrene, propenylbenzene, cyclooctadiene-1,5. The complexes based on β,β'-iminodipropionitrile ligands showed the highest activity. All catalysts can be easily separated from product and used repeatedly without decrease of activity.

INTRODUCTION

Water-soluble metal-complex catalysts have been of great interest in recent years (Ref.1). Aqueous catalysis has considerable unexplored potential. One of the first practical applications of the aqueous catalysts was the rhodium-catalysed hydroformylation of propene using sulfonated triphenylphosphine ligands (Ref.2)

Of special interest is the use of such catalysts in reactions where one of the reactants is water. An example of such a reaction is the Wacker oxidation of alkenes in the presence of palladium(II) catalysts and copper cloride as cocatalyst (Ref. 3). Because of low reaction rates, higher alkene oxidation must be performed at high temperatures, in organic solvents such as *N,N*-dimethylformamide (Ref. 4), etc. In Wacker oxidation, various phase-transfer catalysts and also insoluble polymer-immobilized palladium-containing catalysts have been employed (Ref. 5).

In this work, we have used palladium complexes as catalysts with water-soluble polymers, specifically, polyethylene oxide and ethylene oxide—propylene oxide block copolymers, that were modified terminally by nitrile-containing ligands:

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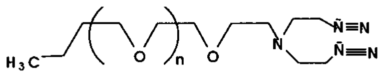
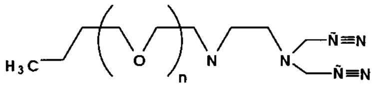
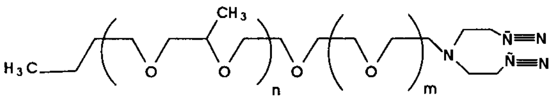


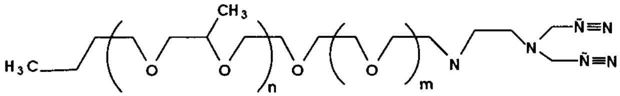
RE-ipn



RE-ian



RPE-ipn



RE-ian

Use of these metal complexes, firstly, allows one to readily separate the reaction products from the catalyst and, secondly, increases the concentration of the organic reactant in the aqueous phase owing to the solubilization of higher hydrocarbon and its transfer into the aqueous phase (Ref. 6).

EXPERIMENTAL

Monobutyl ethers of polyethylene oxide RE (where R = $\mathbf{C_4H_9}$ and E = $\mathbf{(—CH_2—CH_2—O)_n}$) and ethylene oxide—propylene oxide block copolymers RPE (where R = $\mathbf{C_4H_9}$, E = $\mathbf{(—CH_2—CH_2—O)_n}$, and P = $\mathbf{(—CH_2—CH(CH_3)—O)_n}$) with the molecular weight 5 000 were used as initial substances. ^{1}H and ^{13}C NMR spectra were recorded with a Varian WXR-400 spectrometer. FTIR spectra were recorded with a Perkin Elmer 2000 Fourier-transform spectrometer. The reaction products were analyzed with a Chrom-5 gas—liquid chromatograph with a 2.5-m-long column with Carbowax 20M as a stationary phase.

Polymer tosylates **RE—Ts** were synthesized according to the literature procedure (Ref. 7). The polymers produced were modified with iminodipropionitrile groups as follows. Iminodipropionitrile (14.3 mmol) and anhydrous sodium carbonate (10 mmol) were added to a benzene solution of polymer tosylate (3 mmol). The mixture was boiled for 2 h. The precipitate that formed was filtered off, the mixture was cooled, and the macroligand was precipitated by adding diethyl ether.

Ethylenediamine-modified polymers were obtained according to a literature method (Ref. 8). From the polymers obtained, ligand RE—ian was synthesized. For this purpose, chloroacetonitrile (3.6 mmol) was added to a solution of ethylenediamine-modified polymer (0.6 mmol) in anhydrous benzene (50 ml). The mixture was stirred for 48 h at room temperature. Next freshly calcined sodium carbonate (0.66 g) was added to the solution, and the latter was boiled for 2 h. The mixture was filtered, and the polymer produced was precipitated by adding diethyl ether.

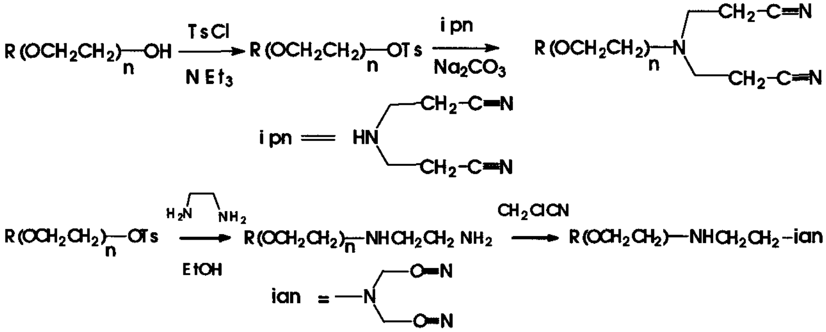
Macromolecular palladium-containing complexes were synthesized by boiling an acetone solution of macroligand (2 mmol) and of anhydrous palladium chloride (2 mmol) for 2 days.

The degree of modification of terminal groups of polymers by nitrile-containing groups was determined from ^1H and ^{13}C NMR spectra. The ^{13}C NMR spectrum exhibited a resonance due to nitrile groups at 118 ppm. The ^1H NMR spectrum displayed resonances at 2.65 and 2.95 ppm that correspond to the methylene protons of iminodipropionitrile groups.

Alkene oxidation by air was carried out in a controlled-temperature catalytic glass reactor that was equipped with a reflux condenser and a trap with a cooling mixture of acetonitrile and liquid nitrogen. The process was conducted in intense stirring at the air flow rate 100—140 ml/min in the temperature range 25—75^{0}C. Alkene oxidation by oxygen was performed in an autoclave at the oxygen pressures in the range 1—3 atm with intense stirring. Copper dichloride was used as a cocatalyst.

RESULTS AND DISCUSSION

Polymer ligands were synthesized according to the scheme



Palladium complexes were studied by FTIR and NMR spectroscopy. The characteristic shift of the absorption band of free ligand from 2221 to 2260 cm^{-1}

indicated the coordination of the nitrile group with the palladium. The shift of the signal of the carbon atom in nitrile groups in the NMR spectrum ranged from 118 to 175 ppm. The palladium content in various samples of catalyst was 1.6 wt %, and the palladium-to-polymer ratio was close to 0.5.

Wacker oxidation of alkenes was carried out both in an air flow at atmospheric pressure, and at oxygen pressures in the range 1—3 atm. in an autoclave. Regularities of the process with the participation of macrocomplexes were studied in case of oxidation of 1-octene and 1-hexadecene (Table 1).

Table 1 Wacker oxidation of hexadecene-1 and octene-1 ($[Pd^{2+}]/[substrate]=1/65$)

Catalyst	Substrate	Oxidant	Time	T,°C	Yield, mol-%	TON
$Pd(ipn)_2Cl_2$	hexadecene-1	air,	5 hr	50	10	12
$RE+Pd(ipn)_2Cl_2$	hexadecene-1	air	5 hr	50	22	26
$RE\text{-}ipn\text{-}PdCl_2$, MM 3000	hexadecene-1	air,	5 hr	45	70	84
		oxygen	2 hr	70	42	128
$RE\text{-}ipn\text{-}PdCl_2$, MM 3000	hexadecene-1	oxygen, 2 atm.	1 hr	70	96	588
	octene-1		4 hr	50	90	138
	hexadecene-1**		1 hr	70	89	545
	hexadecene-1***		0.5 hr	70	98	1200
$RPE\text{-}ian\text{-}PdCl_2$, MM 3000	hexadecene-1	oxygen	4 hr	70	84	128
	octene-1	2 atm.	2 hr	70	64	196

* TON - turnover number, (mmol of product)/ (g-Pd hr)

*** Second test*

****$[Pd^{2+}]/[RE\text{-}ipn] = 0.1$; $[Pd^{2+}]/[substrate] = 1/325$*

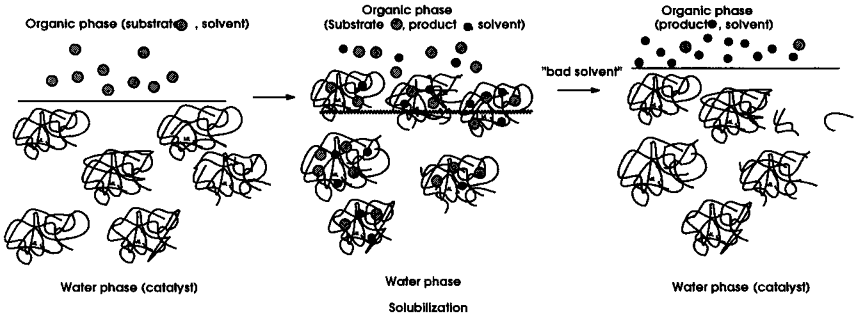
The macrocomplexes produced turned out to be highly active in Wacker oxidation of these compounds. The oxidation proceeded with ethanol—water mixtures as solvents, and in the absence of a solvent.

The higher activity of the supported catalyst in comparison with traditional low-molecular systems seems to be due to the transfer of the substrate into the aqueous phase since the reactant is solubilised in the polymer aggregates.

This observation was corroborated by experiments with mixtures of a low-molecular analoguef iminodipropionitrile complex with polyethylene oxides.

It was shown that the chosen substrate in the presence of macromolecular metal complexes can be oxidized to the corresponding methyl ketones inuantitave yield. The use of oxygen instead of air considerably increased the rate of the oxidation. Iminodipropionitrile-modified complex based on polyethylene oxide exhibited the maximum activity.

The other advantage of the macromolecular catalyst in comparison to low-molecular analogues is the possibility of separating and reusing the catalyst virtually without loss of its activity. The scheme for such a process is shown below.



The substrate is solubilized by the macromolecular complex and passes into the water-phase where the reaction occurs. By adding «bad solvent» (ether), the catalyst can be separated readily from the reaction products and reused. The reaction products remain in the ether solution, and the catalyst is retained in the aqueous phase.

The reaction rate and the yield of ketone increased with temperature rise up to 75^0C (Fig.1). A further increase in temperature decreased the reaction rate. The reaction activation energy was about 50 kJ/mol, which indicates that the reaction occurs in a polymer aggregate in solution.

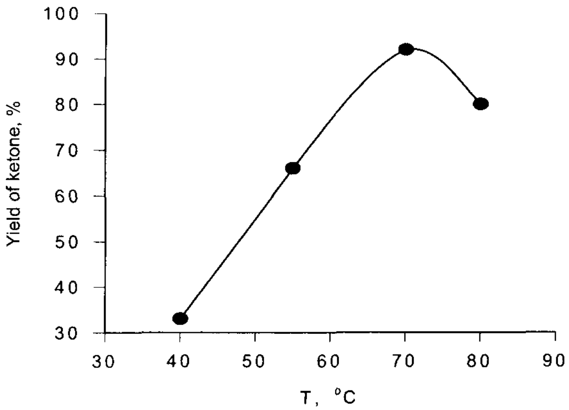


Fig.1. Wacker-oxidation of hexadecene-1 under different temperatures. ($[Pd^{2+}]/[substrate]=1/65$, $Po_2=2$ atm.)

The activity of the catalyst is a maximum when the polymer/Pd^{2+} ratio is 1/6—1/7 (Fig.2) . The higher reaction rate for higher alkenes is caused by the reactant concentration in the polymer aggregates.

It was of interest to study the activity of the catalysts in oxidation of various unsaturated compounds. Allyl benzene, propenyl benzene, styrene, and 1,5-cyclooctadiene were used as substrates. The rates of oxidation of styrene and propenyl-benzene were comparative-ly low because of conjugation of the double bond with the benzene ring. Under the reaction conditions, cyclohexene was almost totally unoxidized,whereas cyclooctadiene was oxidized to ketone.

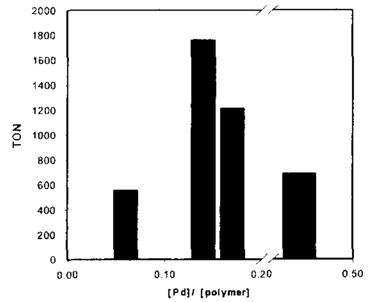
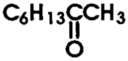
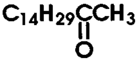
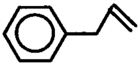
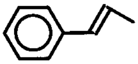
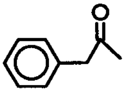
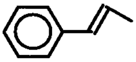
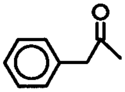
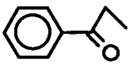
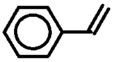
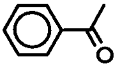
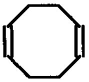
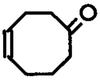


Fig. 2. Effect of Pd^{2+}/polymer ratio on catalyst activity

Table 2 Wacker oxidation of different alkenes.RE-ipn-PdCl$_2$ (MW 3000), T=70^{o}C, H$_2$O/C$_2$H$_5$OH, [Pd^{2+}]/[substrate]=1/65

Substrate	Reaction time, hr.	Product	Yield, mass-%
$C_6H_{13}CH{=}CH_2$	4	 $C_6H_{13}\underset{\underset{O}{\Vert}}{C}CH_3$	88
$C_{14}H_{29}CH{=}CH_2$	2	 $C_{14}H_{29}\underset{\underset{O}{\Vert}}{C}CH_3$	92
	4	 	94 5
	4	 	43 8
	4	 polysterene	48 4
	4	 cyclooctadiones	45 8

Note that isomerization was observed for only allyl benzene. Under the reaction conditions allyl benzene transformed into propenyl benzene almost quantitatiely.

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