Surface Active Macromolecular and Supramolecular Complexes: Design and Catalysis

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SUMMARY: A number of macromolecular and supramolecular catalysts which combine the functions of transition metal complex, phase transfer agent with molecular recognition ability has been designed. The complexes of rhodium, palladium, iron and copper showed the remarkable activity in hydroformylation, Wacker-type oxidation of various olefins, oxidation of alkanes and hydroxylation of aromatics.

Introduction

The development of metal-complex catalysts which allow performing reactions in aqueous media and are readily separated from reaction products has been attracting great attention since Kuntz used sulfonated triphenylphosphine ligands in rhodium catalysed alkene hydroformylation[1-2]. A large number of water-soluble ligands has been synthesized including those containing sulfonate[1-2], carboxylate[3], ammonium groups[4], and also those based on water-soluble polymers[5-7]. These catalysts were studied in many reactions: hydroformylation, hydrogenation, carbonylation and oxidation[8].

After completion of a reaction in water-organic two-phase system the catalyst and reaction product are located in different phases: the product is situated in the organic phase, whereas the catalyst remains in the aqueous phase and can be reused by simple phase separation. While conducting a reaction in a homogeneous water-containing medium (e.g., in the water—alcohol system) the catalyst can be removed from the reaction products by adding an organic solvent that dissolves the reaction products, but does not dissolve the catalyst.

It should be stressed that for reactions with hydrophobic substrates with low solubility in water a metal complex catalyst should be surface-active which makes the addition of phase-transfer agents needless. Therefore, we consider that one of the promising trends in devising surface active water-soluble catalysts is an integration of the properties of a metal complex and a surfactant within a single molecule. One of the successful ways of creating such catalysts is the use of macromolecular ligands based on water-soluble polymers, such as polyethylene oxides and ethylene oxide-propylene oxide block copolymers with high surface

activity. The simplicity of modification of terminal hydroxyls with different groups enabled us to synthesize a number of highly active water-soluble catalysts for various reactions.

Catalyst	Reaction
Complexes based on soluble polymers	
$(RE_{111}PPh_2)_2Rh(acac)$, $(RE_{111}OPPh_2)_2Rh(acac)$, $((RE_{111}O)_2PPh)_2Rh(acac)$, $((RP_{22}E_{88}O)_2PPh)_2Rh$ $(acac)$, $((RE_{88}P_{22}O)_2PPh)_2Rh (acac)^{1)}$	*Hydroformylation*
RE_{111}-acac-Fe^{3+}, $RE_{22}P_{88}$acac-Fe^{3+}, $RP_{88}E_{22}$acac-Fe^{3+}	*Oxidation of cyclohexane, by H_2O_2*
RE_{111}-acac-Co^{2+}, RE_{67}-acac-Co^{2+}, RE_{67}-acac-Cu^{2+}, RE_{111}-acac-Ni^{2+}	*Oxidation of cyclohexane, cyclohexene, epoxidation of cyclohexene by O_2*
RE_{67}-cat-Fe^{3+}, $RE_{54}P_{10}$-cat-Fe^{3+}, $RP_{10}E_{54}$-cat-Fe^{3+}	*Hydroxylation of phenol and benzene*
$(RE_{67}-N(CH_2CH_2CN)_2)_2PdCl_2$ $(RP_{10}E_{54}- N(CH_2CH_2CN)_2)_2PdCl_2$	*Wacker-type oxidation*
Complexes based on β-cyclodextrin	
$(PhCN) (\beta\text{-}CD\text{-}CH_2CH_2CN)PdCl_2$	*Wacker-type oxidation*
$\beta\text{-}CD\text{-}cat\text{-}Fe^{3+}$, $\beta\text{-}CD\text{-}Cu^{2+}$, $E_{50}\text{-}\beta\text{-}CD\text{-}Fe^{3+}$	*Hydroxylation of phenol and benzene*

[1)] E- -OCH_2CH_2; P- -$OCH_2CH(CH_3)$-; acac- acetylacetone, cat – catechol.

   The fact that these polymers are conformationally sensitive and can form different supramolecular structures in aqueous solutions allows one to regard catalysts based on these polymers as supramolecular ones.

   Another class of macromolecular ligands which seem highly attractive for devising water-soluble supramolecular catalysts is modified cyclodextrins. α-, β- and γ-Cyclodextrins (CD) are cyclic oligosaccharides contsisting of six, seven, and eight α-D-glucose units. Owing to the hydrophobic cavity of appropriate size cyclodextrins can form host—guest supramolecular complexes in aqueous solutions with nonpolar organic molecules, such as benzene or 1-octene. Nonmodified CD have been used in catalytic reactions in conjunction with water-soluble metal complexes as phase-transfer agents [9].

   Metal complexes based on modified cyclodextrins combine the properties of a metal complex and a phase-transfer agent with molecular recognition ability. In the present work, we explored iron and copper complexes with modified β-cyclodextrins (β-CD) in hydroxyla-

tion of aromatic substances and Wacker oxidation of unsaturated compounds.

Experimental

Polymers modified by acetylacetone groups (RE_{111}-acac, RE_{67}-acac, $RP_{10}E_{54}$-cat, $RP_{88}E_{22}$acac) and by catechol groups (RE_{67}-cat, $RE_{54}P_{10}$-cat, $RP_{10}E_{54}$-cat) were synthesized from the corresponding tosylates according to the procedures from[10-11]. Polymer ligands $RE_{111}PPh_2$, $RE_{111}OPPh_2$, $(RE_{111}O)_2PPh$, $(RP_{22}E_{88}O)_2PPh$, $(RE_{88}P_{22}O)_2PPh$ were prepared according to the literature procedure[5]. Oxyethylated β-cyclodextrin (E-β-CD) was synthesized by ethylene oxide oligomerization in the presence of β-cyclodextrin (β-CD)[12]. ^1H 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 degree of modification of terminal hydroxyls of polymers was determined from ^1H and ^{13}C NMR spectra:

The β-CD-CH_2CH_2CN ligand was obtained as follows. To the solution, prepared from β-cyclodextrin (11.3 g, 10 mmol) and 5 ml of 10%NaOH, acrylonitryl (0.66 ml, 10 mmol) was added in stirring at 55 ^{o}C. The mixture was stirred for 30 min and then was poured in 300 ml of methyl alcohol. White precipitate was collected, dried and recrystalised from hot methanol. NMR ^1H spectra: 3.19-3.27ppm; 3.51-3.9ppm; 4.5-4.7 ppm – H β-CD; 3.47ppm, 3.38 ppm –H CH_2CH_2CN, NMR ^{13}C spectra –118-119 ppm CN; FTIR. 2255 - ν CN

The β-CD -cat ligand was prepeared using dicyclohexylcarbodiimid. Solution of β-cyclodextrin in 25 ml DMFA was added to solution of 3,4-dihydroxybenzoic acid (2.5 mmol) and dicyclohexylcarbodiimid (5 mmol) in 75 ml DMFA. The solution was stirred for 4 h. under room temperature, then acetone (250 ml) was added. The precipitate was separated, washed with acetone and dried. NMR ^1H spectra:8 ppm, 7.3 ppm, 6.8 ppm - catechol group; 3.2-3.7 ppm, 4.8 ppm - β-CD; NMR ^{13}C spectra – 114, 120, 143, 148 ppm – C catechol.

The oxidation of cyclohexene, ethylbenzene, hydroxylation of phenol and benzene was performed both in homogeneous and heterophase systems using glass thermostatic reactor. The epoxidation of cyclohexene, Wacker-type oxidation of hydrocarbons, hydroformylation was performed in an autoclave Products were analyzed by GCS on a Chrom-5 gas chromatograph and by HPLC on Gilson- 310 and further characterised by GS-MS using a Finnigan-MAT-1125 GC/MS system.

Results and discussion

1. Hydroformylation.   Rhodium complexes based on polyethylene oxides modified by phosphorus-containing groups were used as catalysts in hydroformylation in two-phase system. Toluene, hexane, and in some cases substrate were used as solvents. The main reaction products were the corresponding aldehydes with the normal and iso-structures (Table 1, Fig.1). A quantitative conversion was achieved within 10-16 h. The activity of catalysts based on block copolymers proved to be lower than that of macromolecular metal complexes based on polyethylene oxide. The macromolecular complex based on the block copolymer wherein rhodium atoms are located in the hydrophobic part of a molecule was more active than the similar catalyst whose active site is in the polar ethylene oxide part.
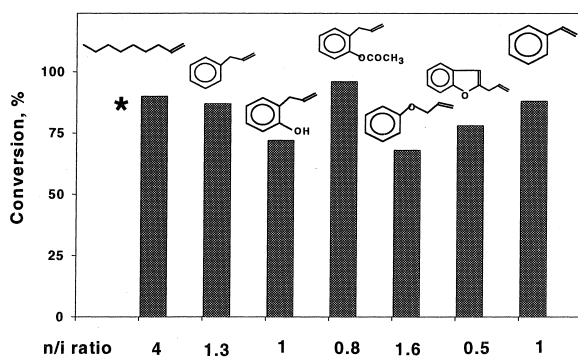
Table 1. Hydroformylation of dodecene-1. Reaction time 6 h., Synthesis-gas pressure 1.5 Mpa T=50°C, water/hexane

Catalyst	Conversion, %	n/i ratio
$(RE_{111}PPh_2)_2Rh(acac)$	45	1.8
$(RE_{111}OPPh_2)_2Rh(acac)$	68	2.1
$((RE_{111}O)_2PPh)_2Rh\ (acac)$	70	2
$((RP_{22}E_{88}O)_2PPh)_2Rh\ (acac)$	43	2.2
$((RE_{88}P_{22}O)_2PPh)_2Rh(acac)$	58	2

Fig.1.   Hydroformylation of olefines. Reaction time 6 h., Synthesis-gas pressure 1.5 Mpa T=50°C, water/hexane, *molar ratio $(RE_{111}O)_2PPh$ /Rh =15

Catalysts based on the ligand that has the strongest electron acceptor power, specifically REOPPh2, exhibited the highest activity. The catalysts could be reused virtually without loss of activity.

2. Cyclohexane oxidation.   Cyclohexane was oxidized by both hydrogen peroxide in water-acetonitrile medium and oxygen in a two-phase system (Table 2). The main reaction products were cyclohexanol and cyclohexanone. In cyclohexane oxidation by hydrogen peroxide the highest activity was displayed by catalysts based on ethylene oxide-propylene oxide block copolymers, with the main reaction product being cyclohexanol. In cyclohexane oxidation oxygen in a two-phase system the major reaction product was cyclohexanone. The degree of substrate conversion reached 15%

Table 2. Oxidation of cyclohexane

Macrocomplex	T, ^{o}C	Oxidant	Product yield	
			cyclohex-anone	cyclo-hexanol
RE_{111}-acac-Fe^{3+}	30	H_2O_2 0.93 mol/l	5	31
$RE_{22}P_{88}$acac-Fe^{3+}	30	H_2O_2 0.93 mol/l	4	49
$RP_{88}E_{22}$acac-Fe^3	50	H_2O_2 0.93 mol/l	2	42
RE_{67}-acac-Co^{2+}	65	O_2, 0.5 Mpa.	14	2
RE_{67}-acac-Cu^{2+}	65	O_2, 0.5 Mpa.	16	2

3. Cyclohexene oxidation **(Table 3).**   Cyclohexene oxidation by oxygen was carried out in the water-substrate two-phase system and in the presence of isobutyraldehyde under Mukaiyama's conditions[13].

Table 3. Oxidation of cyclohexene

Macrocomplex	T, ^{o}C	Oxidant	Reaction time, h	Product
RE_{67}-acac-Ni^{2+}	25	O_2, 0.25 Mpa*,	8	64 % epoxycyclohexane
RE_{67}-acac-Co^{2+}	25	O_2, 0.25 Mpa *	8	54 % epoxycyclohexane
RE_{67}-acac-Co^{2+}	65	O_2, 0.5 Mpa Water	2	21% cyclohexanone 4% cyclohexanol
RE_{67}-acac-Cu^{2+}	65	O_2, 0.5 Mpa. Water	2	24% cyclohexanone 6% cyclohexanol

* coreactant - isobutyraldehyde.

In cyclohexene oxidation by oxygen in the two-phase system the reaction products were

cyclohexenol and cyclohexenone, of which the major product was cyclohexenone. In cyclo-hexene oxidation in the presence of isobutyraldehyde, the main product was epoxide whose yield under optimal conditions, was about 65%.

4. Benzene and phenol hydroxylation. Hydroxylations of benzene (Table 4) and phenol (Table 5) by hydrogen peroxide catalysed by macromolecular iron complexes in the water-acetonitrile medium and also iron and copper β-CD-based complexes in a two-phase system have been studied. While conducting reaction using polyether based macromolecular complexes the phenol yield was 30% . The yields of dihydroxybenzenes were insignificant.

Table 4. Hydroxylation of benzene by H_2O_2, T=50°C

Catalyst	Solvent	Reaction		Yield, %	
		time	phenol	Hidroquinone	Catechol
RE_{67}-cat-Fe^{3+}	$CH_3CN/H_2O=4$	45 min	34	2	5
$RE_{54}P_{10}$-cat-Fe^{3+}	$CH_3CN/H_2O=4$	45 min	22	3	5
$RP_{10}E_{54}$-cat-Fe^{3+}	$CH_3CN/H_2O=4$	45 min	16	1	4
E_{50}-β-CD-Fe^{3+}	H_2O	60 min	69	6	1
β-CD-cat-Fe^{3+}	H_2O	60 min	25	1	16
β-CD /Cu^{2+}	H_2O	120 min	7	3	3

Ethoxylated β-cyclodextrin, which is not only surface-active, but also can form host-guest compounds, was used as ligand for preparing in situ iron complexes. In this case the phenol yield reached 70% in 30 minutes. In reaction catalysed by iron complex with catechol modified β-CD the major reaction product was catechol.

Table 5. Hydroxylation of phenol by H_2O_2, 50 $^{\circ}$C, ([H_2O_2]= 0.1mol/L , [M^{2+}]= 0.5 mmol/L), [C_6H_5OH]= 0.05 mol/L)

Catalyst	T, $^{\circ}$C	Reaction	Phenol con-	Yield	
		time, min	version, %	Hydroquinone	Catechol
RE_{67}-cat-Fe^{3+}	50	30	85	25	54
β-CD-cat-Fe^{3+}	20	150	85	3	81
β-CD-cat-Fe^{3+}	40	90	79	7	72
E_{50}-β-CD-Fe^{3+}	50	60	45	41	4
β-CD /Cu^{2+}	40	30	99	<1	98
β-CD /Cu^{2+}	50	30	95	<1	94

In phenol hydroxylation a substantial difference in selectivity was observed. In the case of polyether-based catalysts the degree of conversion reached 70% at catechol-to-hydroquinone ratios from 2.8:1 to 3:1. In the presence of ethoxylated β-CD based catalyst, the conversion was somewhat lower, but the main and virtually unique reaction product was hydroquinone. With unmodified β-CD complex the catechol-to-hydroquinone ratio was 1:1.6. At the same time, in the cases of iron and copper macromolecular complexes with modified β-CD, the phenol conversion was shown to be close to 95%, the selectivity with respect to catechol being almost quantitative. We relate this abrupt change in the selectivity to the "double recognition" effect[14]. In formation of a host—guest complex phenol additionally binds with the metal ion thus increasing considerably the stability of the complex. Using HPLC as proposed in [15], we found that the stability constants of host-guest complexes of phenol sharply increase in the order: **β-CD<<β-CD-cat-Fe^{3+}<β-CD-Cu^{2+}**, whereas those for hydroquinone and catechol varied only to a small extent. In this coordination the para- position of a substrate molecule is inaccessible to hydroxylation, whereas the ortho- position in the inclusion complex becomes open to attack.
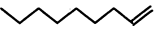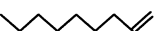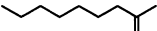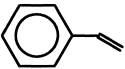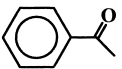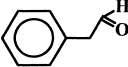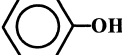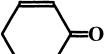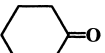
5. Wacker oxidation of alkenes. Wacker oxidation of alkenes was catalysed by macromolecular metal complexes based on polyethylene oxide and ethylene oxide-propylene oxide block copolymers modified with iminodipropionitrile and also by monocyanoethyl ether of β-CD and ethoxylated β-CD under oxygen pressures of 2-5 atm (Table 6).

The major reaction products were the corresponding ketones, activity of β-CD-based catalysts considerably exceeding that of polyether-based catalysts. Note that the activity of all of the catalytic systems was higher than that of analogous mixture catalysts. This is explained by the diminution in the activation entropy owing to the fact that a fragment (polymer or β-CD) binding a substrate and transferring it into the aqueous phase and a metal site are combined within the same molecule. The higher activity of the catalytic system based on ethoxylated β-CD is due to the higher surface activity of the catalyst. A greater activity of the catalyst based on cyanoethyl ether of β-CD can also be attributed to the double recognition effect, which was already revealed in hydroxylation (see above), and to the rise in the stability constant of the inclusion complex.

It should be emphasized that this catalyst is characterized by an unusual selectivity with respect to substrates other than higher alkenes. In Wacker oxidation of styrene, along with acetophenone, phenylacetaldehyde was formed. Of greatest interest is cyclohexene oxidation,

which is similar to cyclohexene oxidation by NADPH enzyme[16]. In this oxidation the main reaction product was phenol, and under the oxygen pressure of 0.2 MPa the selectivity with respect to this product was almost quantitative. It was shown that under the same conditions cyclohexen-2-on converts completely to phenol. The host molecule apparently stabilises the enol form of cyclohexen-2-on.

Table 6. Wacker-type oxidation of unsaturated compounds.

Catalyst	T, C	P, MPa	Substrate	Product	Yield, %
$(RE_{67}\text{-}N(CH_2CH_2CN)_2)_2PdCl_2$	50	2			90
$(RP_{10}E_{54}\text{-}N(CH_2CH_2CN)_2)_2PdCl_2$	50	2			74
$(PhCN)(\beta\text{-}CD\text{-}CH_2CH_2CN)PdCl_2$	60	5			97
$(PhCN)(\beta\text{-}CD\text{-}CH_2CH_2CN)PdCl_2$	60	5			37
					51
$(PhCN)(\beta\text{-}CD\text{-}CH_2CH_2CN)PdCl_2$	60	5			65
					12
					19

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