SUPRAMOLECULAR METALCOMPLEX CATALYTIC SYSTEMS ON THE BASE OF OIL PORPHYRINS FOR ALKENES OXIDATION

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The cobalt-porphyrin complex modified by oligomer crown compounds has been obtained on the basis of oil-metalporphyrin concentrate. Synthesized complex possesses supramolecular catalytic properties. It is found that the resulting catalyst system is effective in the oxidation of alkenes and unsaturated organic compounds.

Keywords: porphyrin complex, crown compounds, clathrate metal complex, oxygenation of alkenes.

Currently a promising direction of highly efficient catalysts development is the application in the catalysis the principles of supramolecular chemistry. Peculiarity of supramolecular chemistry is the study organized molecular systems held by nonvalent molecular forces [1].

It particularly concerns the macrocyclic metal complex systems having the ability of molecular recognition [2]. Modification of metal catalytic systems by introducing macrocyclic receptor undoubtedly became a new way in catalysis, as these systems are superior several times existing catalysts on selectivity. Considering the factor of selectivity, the most important in the chemical industry is the use of catalytic systems having molecular recognition ability.

Therefore cobalt porphyrin complex CoII P obtained on the basis of oil porphyrin concentration is modified by crown compound II [4] obtained oligomerization of 15-glycidyl-oxy-2,3,11,12-dibenzo-16-crown:

Since the crown-oligomeric compound II \( n=2-4 \) has a cylindrical cavity, they involve a cobalt porphyrin complex in its cavity and cobalt porphyrin complex I is retained there in by nonvalent forces. It results to formation of clathrate metal porphyrin complex III where one tetramer crown compound has two cobalt atoms.

where P – porphyrin.
It should be noted that the cobalt porphyrin complex CoP is located between the planes of polyester rings of tetramer crown compound II.

The reactions of 1-alkenes oxygenation tetramer crown compound II acts as a macromolecular receptor capable to place in one cavity ("microreactor") cobalt porphyrin complex I, substrate and oxygen.

Biphasic Wacker oxidation of 1-alkenes to ketones catalyzed by systems based on cobalt(II) chloride and tetramer 15-glycidyloxy-2,3,11,12-dibenzo-16-crown-5 (II) has been studied. In this case, the resulting clathrate complex crown compound II \((n=4)\) with 1-alkene is transferred into the aqueous phase where oxygenation reaction takes place:

\[
R\text{CH}=\text{CH}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \rightarrow R\text{C}=\text{CH}_3.
\]

Adding of oligomeric crown compound II in the optimum amount increases the rate of oxidation of the 1-alkene more than 15 times. Thus, the initial reaction rate of the oxidation of 1-hexene using tetrameric crown compound (II, \(n=4\)) is more than four times higher than in the case of dimeric crown compound (II, \(n=2\)). Obviously the difference in activity is related to the stability of the corresponding clathrate complexes "guest-host", generated with substrates. With the crown compound monomer (II, \(n=1\)) the clathrate complex formation is complicated because of its relatively small internal cavity; tetramer crown compound (II, \(n=4\)) has too large cavity, so that the complex is unstable. It is remarkable that the oxygenation of 1-alkenes was processing regioselectively carbonyl group is usually in the position C2, despite the presence in the reaction mixture isomeric alkenes with interval multiplicity of bond. Oxygenation rate of the latter is very low, due to the structure of the corresponding clathrate complex; double bond in alkenes is located within the cavity and the crown compound is not available for reaction.
Experimental part

Mono-, di- and tetramer crown compounds obtained on the basis of hydroxy-2,3,11,12-dibenzo-16-crown-5 (I) [4].

Monomeric crown compound (II, n=1) is obtained are used in the work on the basis of 16-hydroxy-2,3,11,12-dibenzo-16-crown-5 [4] by treating it with epichlorohydrin in the presence of KOH+CaO mixture.

DimERIC and tetrameric crown ethers (II, n=2 and II, n=4) were obtained by oligomerization of epoxy substituted crown compound (I). For this purpose 0.5 ml of boron trifluoride eluent was added to 0.2 M ether solution of epoxy-substituted crown ether by stirring at room temperature. Stirring was continued for another 2 hours. After the reaction, ether was removed and the residue was chromatographed in a glass column: height – 1.2 m, diameter – 1.5 cm, adsorbent – Al₂O₃ II activity level, eluent – mixture of acetone and n-hexane in volume ratios of 1:1.5. Dimeric crown ether (II, n=2) was separated with 17% yield, melting point is 53–54°C and tetrameric crown ether (II, n=4) with 32% yield, melting point – 73–75°C. Elemental analysis results confirm the assigned structure and compositions of isolated compounds.

Cobalt porphyrin complex I is derived from petroleum porphyrin concentrate on the developed method described in [3].

Analysis of the initial materials and reaction products were performed by gas-liquid chromatography. Obtained methyl ketones are identified by GLC and IR spectroscopy. The catalytic system is characterized by IR spectroscopy.

The experimental data obtained for 1-alkenes oxygenation are shown in the Table.

Catalytic oxidation of 1-alkenes was carried out in an autoclave with glass insert as following.

Oxygenation of 1-alkenes, catalyzed by oil cobalt porphyrin complex, modified by oligomeric crown compounds; T=60°C, P₀₂=0.1 MPa, [CoP]=2 mmol/l, ratio[CoP]·[crown ether]:[1-alkene]=1:4:1000

<table>
<thead>
<tr>
<th>1-alkenes</th>
<th>Yield of ketone, wt.%</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>monomer crown ether II, n=1</td>
</tr>
<tr>
<td>1-pentene</td>
<td>1.2</td>
</tr>
<tr>
<td>1-hexene</td>
<td>1.4</td>
</tr>
<tr>
<td>1-octene</td>
<td>1.1</td>
</tr>
<tr>
<td>1-decene</td>
<td>0.9</td>
</tr>
<tr>
<td>1-dodecene</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Solution of the calculated amount of cobalt chloride in water (pH=3), oil porphyrin, a monomeric or oligomeric crown compound and the substrate were placed into the autoclave. Autoclave was controlled at selected temperature, then oxygen (0.1 MPa) was inflected into it. After the reaction products were extracted with ether and analyzed by GLC. Analysis was carried out using a chromatograph LHM-8MD, SE-30 column (0.3 mm by 30 m) at a programmed temperature from 40 to 200°C with a heating rate of 10°C per minute.

References

4. Агагусеянова М.М., Джаббарова Н.Э. Координационные соединения переходных металлов в катализе. Баку: Элм, 2006. 244 с.
На основе нефтяного металлопорфиринового концентрата получен модифицированный олигомерно краун-соединениями кобальтпорфириновый комплекс, обладающий супрамолекулярным катализитическим свойством. Установлено, что полученная каталитическая система является эффективной в реакции окисления алканов и ненасыщенных органических соединений.

Ключевые слова: порфириновые комплексы, краун-соединения, клатратные комплексы металла, окисление алканов.