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CROWN ESTERS IMMOBILIZED ON POLYMERIC SUPPORTS AS NOVEL INTERFACIAL CATALYSTS

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Abstract. This work proposes a new approach to the preparation of efficient crown-ether-containing phase-transfer catalysts. Phase-transfer catalysis is an effective method for intensifying organic reactions and is widely used in fine organic synthesis and polymer chemistry. Of particular interest are polymer-supported phase-transfer catalysts that combine the high catalytic activity of crown ethers with the advantages of heterogeneous systems, including regeneration, and applicability in continuous processes. The influence of the polymer matrix structure and the degree of immobilization of active sites on the catalytic properties remains insufficiently studied. The aim of this work is the immobilization of benzo-derived crown ethers on anion exchangers with different morphologies and the investigation of their catalytic activity under phase-transfer catalysis conditions. The immobilization of chlorosulfonyl derivatives of benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6 was carried out on AN-15, AN-21, and AN-22 anion exchangers in organic solvent media. The obtained

materials were characterized by IR spectroscopy and elemental analysis. Catalytic activity was evaluated in the nucleophilic substitution reaction of n-butyl bromide under heterogeneous conditions. It was established that the degree of immobilization and catalytic activity depend on the structure of the polymer support, the degree of crosslinking, and the content of crown-ether groups. The results demonstrate that the activity of immobilized crown-ether catalysts is governed by multiple factors, among which the most important are the amount of crown-ether groups and the composition and structure of the polymer matrix, which determine the swelling of the support and the accessibility of active sites. The obtained results can be used in the development of efficient and regenerable phase-transfer catalysts for organic and industrial synthesis.

Keywords: Crown ether, interphase catalyst, ion exchangers, model carrier

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ПОЛИМЕРЛІК ТАСЫМАЛДАУШЫЛАРДА ИММОБИЛИЗАЦИЯЛАНҒАН КРАУН-ЭФИРЛЕР — ЖАҢА ФАЗААРАЛЫҚ КАТАЛИЗАТОРЛАР РЕТІНДЕ

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Аннотация. Бұл жұмыста тиімді краунқұрамды фазааралық катализаторларды алудың жаңа әдісі ұсынылады. Фазааралық катализ органикалық реакцияларды қарқынды жүргізудің экологиялық тұрғыдан тиімді әдісі болып табылады және органикалық синтезде және полимерлік химияда кеңінен қолданылады. Әсіресе,

краун-эфирлердің жоғары каталитикалық белсенділігін гетерогенді жүйелердің артықшылықтарымен, атап айтқанда регенерациялау, қайта пайдалану және үздіксіз процестерде қолдану мүмкіндігімен үйлестіретін полимерлі тасымалдағыштағы межфазалық катализаторлар үлкен қызығушылық тудырады. Сонымен қатар, полимерлі матрицаның құрылымы мен белсенді орталықтардың иммобилизация дәрежесінің каталитикалық қасиеттерге әсері жеткілікті дәрежеде зерттелмеген. Жұмыстың мақсаты - әртүрлі морфологиялы аниониттерге бензотуынды краун-эфирлерді иммобилизациялау және олардың фазааралық катализ жағдайындағы каталитикалық белсенділігін зерттеу. Зерттеу әдістері. Бензо-12-краун-4, бензо-15-краун-5 және бензо-18-краун-6 хлорсульфонил туындыларын иммобилизациялау АН-15, АН-21 және АН-22 аниониттерінде органикалық еріткіштер ортасында жүргізілді. Алынған материалдар ИҚ-спектроскопия және элементтік талдау әдістерімен зерттелді. Каталитикалық белсенділік н-бутилбромидтегі нуклеофильдік орынбасу реакциясында гетерофазалық жағдайларда бағаланды. Иммобилизация дәрежесі мен каталитикалық белсенділік полимерлі тасымалдағыштың құрылымына, тігілу дәрежесіне және краун-эфир топтарының құрамына тәуелді екені анықталды. Алынған нәтижелер иммобилизацияланған краун-эфирлі катализаторлардың белсенділігі көптеген факторларға байланысты екенін көрсетті, олардың ішінде ең маңыздылары — краун-эфир топтарының мөлшері, тасымалдағыштың ісінуін және белсенді орталықтардың қолжетімділігін анықтайтын полимерлі матрицаның құрамы мен құрылымы болып табылады. Алынған нәтижелер органикалық және өнеркәсіптік синтезге арналған тиімді әрі регенерацияланатын межфазалық катализаторларды әзірлеуде қолданылуы мүмкін.

Түйін сөздер: краун-эфир, фазааралық катализатор, иониттер, полимерлі тасымалдағыш

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КРАУН-ЭФИРЫ, ИММОБИЛИЗОВАННЫЕ НА ПОЛИМЕРНЫХ НОСИТЕЛЯХ, КАК НОВЫЕ МЕЖФАЗНЫЕ КАТАЛИЗАТОРЫ

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Аннотация. В работе предложен новый способ получения эффективных межфазных краунсодержащих катализаторов. Межфазный катализ представляет собой экологически ориентированный и высокоэффективный метод интенсификации органических реакций, широко применяемый в тонком органическом синтезе и полимерной химии. Особый интерес вызывают полимерно-иммобилизованные катализаторы межфазного переноса, сочетающие высокую каталитическую активность краун-эфиров с преимуществами гетерогенных систем, такими как возможность регенерации, многократного использования и применения в непрерывных технологических процессах. Вместе с тем влияние структуры полимерной матрицы и степени иммобилизации активных центров на каталитические свойства таких систем остаётся недостаточно изученным. Целью работы является иммобилизация бензо-производных краун-эфиров на анионитах различной морфологии и исследование их каталитической активности в условиях межфазного катализа. Иммобилизацию хлорсульфонильных производных бензо-12-краун-4, бензо-15-краун-5 и бензо-18-краун-6 осуществляли на анионитах АН-15, АН-21 и АН-22 в среде органических растворителей. Полученные материалы были исследованы методами ИК-спектроскопии и элементного анализа, что позволило подтвердить успешность иммобилизации и определить состав полученных соединений. Каталитическую активность синтезированных систем оценивали в реакции нуклеофильного замещения н-бутилбромида в гетерофазных условиях. Установлено, что степень иммобилизации и каталитическая активность существенно зависят от структуры полимерного носителя, степени его сшивки и содержания краун-эфирных групп. Показано, что каталитическая активность иммобилизованных краун-эфирных систем определяется совокупностью факторов, среди которых ключевыми являются концентрация активных центров, состав и морфология полимерной матрицы, влияющие на набухаемость носителя и доступность реакционных центров. Полученные результаты демонстрируют перспективность использования синтезированных материалов в качестве эффективных и регенерируемых катализаторов межфазного переноса для органического и промышленного синтеза.

Ключевые слова: Краун-эфир, межфазный катализатор, иониты, проимерный носитель

Introduction. High complexing ability and catalytic activity of polymers containing crown ether groups determine their wide application in interphase catalysis. These systems provide several important advantages, including simplicity of implementation, reduced consumption of organic solvents, mild reaction conditions, high selectivity, and the ability to control both reaction conditions and rates. Interphase (phase-transfer) catalysis is considered an environmentally friendly approach due to reduced waste

generation, replacement of hazardous reagents (e.g., sodium hydride) with safer aqueous bases (e.g., sodium hydroxide), and the use of more sustainable solvents.

Despite the extensive application of interphase catalysts in industrial and laboratory processes, polymer-supported systems (three-phase catalysts) remain insufficiently studied and have not yet achieved wide industrial implementation. At the same time, such systems combine the advantages of heterogeneous catalysis, including easy separation from the reaction mixture, reusability, and suitability for continuous processes. Therefore, the development of efficient polymer-supported interphase catalysts based on crown ethers remains a relevant scientific and practical task.

The aim of this work is to immobilize crown ethers on polymer carriers and to study their catalytic activity under interphase catalysis conditions.

Literary review. The concept of phase-transfer catalysis was first introduced by Starks in 1971 to explain the role of catalysts in reactions occurring between reagents located in immiscible phases (Demlov, 1987; Hashimoto et al., 2007). Since then, this methodology has become widely used in both academic research and industrial applications. Phase-transfer catalysis has found applications in the synthesis of fine chemicals, including flavorings, pharmaceuticals, agrochemicals, and polymers, as well as in large-scale industrial processes (Ooi et al., 2007; Starks et al., 2012).

Various types of interphase catalysts have been developed, including quaternary ammonium and phosphonium salts, crown ethers, and cryptands (Ford et al., 1984; Makosza et al., 2003; Makosza et al., 2020; Cozzi, 2006). Among them, quaternary ammonium salts are the most widely used due to their low cost and availability. Special attention has been given to crown ether-based catalysts due to their high complexing ability toward metal cations, which significantly enhances catalytic efficiency in organic reactions (Ergozhin et al., 1994; Ergozhin et al., 1995; Dong et al., 2013; Duan et al., 2022).

In recent years, increasing interest has been focused on polymer-supported phase-transfer catalysts, which combine the high activity of homogeneous catalysts with the operational advantages of heterogeneous systems. The most commonly used polymer supports include polyethylene glycol and crosslinked polystyrene based on divinylbenzene (Lu et al., 2009; Benaglia et al., 2003; Shuangshuang et al., 2022). Such catalysts have been successfully applied in various organic transformations, including esterification, amidation, polymerization, and the synthesis of α-amino esters (Siewniak et al., 2022; Rosaria et al., 2024). However, the influence of the polymer matrix structure, degree of crosslinking, and immobilization of active centers on catalytic performance remains insufficiently understood.

Materials and methods. Anion exchangers AN-15, AN-21, and AN-22 based on styrene–divinylbenzene copolymers were used as polymer supports. These ion-exchange resins were manufactured by the Cherkasy Chemical Plant (Ukraine) and differed in their structural characteristics, including the degree of crosslinking and morphology (gel, macroporous, and macroreticular types). Prior to use, the anion exchangers were washed successively with distilled water and organic solvents to remove residual impurities and then dried to constant weight.

Benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6 (Kente, China) were used as initial macrocyclic compounds. Their chlorosulfonyl derivatives — 4'-chlorosulfonylbenzo-12-crown-4 (CSB12C4), 4'-chlorosulfonylbenzo-15-crown-5 (CSB15C5), and 4'-chlorosulfonylbenzo-18-crown-6 (CSB18C6) — were synthesized according to the method previously described by Ergozhin et al. (1991). These derivatives contain reactive chlorosulfonyl groups, which enable covalent immobilization onto polymer matrices.

The immobilization of crown ether derivatives onto anion exchangers was carried out in an organic solvent medium. Typically, a known amount of the anion exchanger was placed in a reaction vessel and swollen in an appropriate solvent (chloroform, dichloromethane, or pyridine) to ensure maximum accessibility of functional groups within the polymer matrix. After swelling, the corresponding chlorosulfonyl derivative of the crown ether was added to the system. The reaction mixture was maintained at a temperature of 50–70 °C under continuous stirring for 24 hours. Pyridine was found to be the most effective solvent, as it not only promotes swelling of the polymer matrix but also acts as an acid acceptor, neutralizing hydrogen chloride released during the reaction. This prevents degradation of the polymer and increases the efficiency of immobilization.

After completion of the reaction, the modified anion exchangers were thoroughly washed with organic solvents and distilled water to remove unreacted reagents and by-products. The samples were then dried to constant weight under vacuum. The degree of immobilization of crown ether groups was evaluated based on the sulfur content determined by elemental analysis, since sulfur is present in the sulfonyl functional group of the immobilized fragment. The content of crown ether groups (mmol/g) and conversion degree (%) were calculated accordingly.

Infrared (IR) spectra of the initial and modified samples were recorded using a "Specord IR-75" spectrophotometer in order to confirm the successful immobilization of crown ether groups. The appearance of characteristic absorption bands corresponding to SO_2 groups (≈1350 and 1150 cm^{-1}), as well as Ar–O–C and C–O–C bonds, was used as evidence of chemical modification. The main physicochemical characteristics of the ion exchangers, including exchange capacity, swelling degree, and structural parameters, were determined according to standard procedures described in (Ergozhin et al., 2020).

Results. Anion exchangers based on styrene-divinylbenzene (DVB) copolymer AN-15, AN-21, and AN-22 were used to fix crown ethers.

Since the structure of the macromolecular network plays an important role in immobilization and use, the polymerization carriers had gel, macroporous, and macromolecular structures with varying crosslinking agent content (1-20 mol%).

In order to regulate the complex-forming properties of catalyst macrocycles with metal ions, chlorosulfonyl derivatives of benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6 were used.

Pyridine proved to be the most suitable solvent, which is simultaneously an acceptor of HCI released during the reaction.

The amount of crown ether groups introduced was judged by the sulfur content. Table

1 shows the results of immobilization of crown ethers on anion exchangers. As can be seen from the table, the reactivity of crown ethers during immobilization is practically the same, and the degree of conversion depends on the structure of the anion exchanger used. Thus, up to 5.4% sulfur can be introduced into macro-mesh anion exchangers, which is 92% conversion, while for gel anion exchangers it is 85.5%. Modified anion exchangers containing 1.45 to 1.92 mmol/g of crown ether groups have a swelling capacity in water of 2.4 to 3.0 g/cm^3.

Table 1 — Data on the immobilization of crown ethers on anion exchangers

Anionite	Copolymer structure	Immobil, crown ether	Sulfur content, %	Conversion rate, %	Crown ether group content, mmol/g
AN -15	Gel	CSB12C4	5,98	80,2	1,85
		CSB15C5	5,40	79,8	1,68
		CSB18C6	4,89	79,0	1,52
	Macropor.	CSB12C4	6,15	82,3	1,92
		CSB15C5	5,51	81,5	1,72
		CSB18C6	5,02	81,0	1,56
AN -22	Gel	CSB12C4	5,57	83,1	1,74
		CSB15C5	5,04	82,7	1,57
		CSB18C6	4,63	82,5	1,44
	Macropor.	CSB12C4	5,79	85,5	1,81
		CSB15C5	5,27	85,2	1,64
		CSB18C6	4,85	84,9	1,52
AN -21	Gel	CSB12C4	5,05	85,6	1,58
		CSB15C5	4,65	85,2	1,45
		CSB18C6	4,32	85,0	1,35
	Macropor.	CSB12C4	5,17	87,6	1,61
		CSB15C5	4,77	87,4	1,49
		CSB18C6	4,43	87,2	1,39
	Macroset.	CSB12C4	5,43	92,0	1,69
		CSB15C5	5,01	91,8	1,56
		CSB18C6	4,66	91,7	1,46

Thus, by using macromolecules with different spatial structures, it is possible to specifically alter the swelling properties of polymers and the accessibility of crown ether groups when using anions as interphase catalysts.

The IR spectra of the modified anion exchangers clearly confirm the successful immobilization of crown ether fragments onto the polymer matrix. In particular, the appearance of characteristic absorption bands corresponding to asymmetric and symmetric stretching vibrations of the sulfonyl (SO_2) group at approximately 1350 and 1150 cm^{-1} indicates the formation of sulfonamide linkages between the chlorosulfonyl derivatives of crown ethers and the functional groups of the anion exchanger.

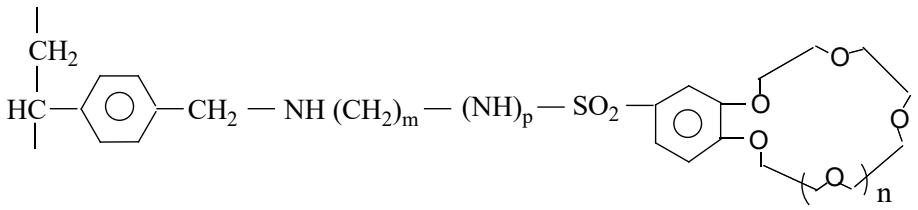
Additionally, the presence of absorption bands in the regions of 1200–1300 cm^{-1} and 1050–1150 cm^{-1} can be attributed to stretching vibrations of Ar–O–C and C–O–C bonds, respectively, which are characteristic of the crown ether macrocyclic structure. The preservation of these bands after immobilization suggests that the macrocyclic cavity of

the crown ether remains intact, which is essential for maintaining its complexing ability toward metal cations.

A slight shift in the position and intensity of these absorption bands, compared to the initial compounds, may be associated with changes in the electronic environment of functional groups due to their incorporation into the polymer matrix. This also indirectly confirms the formation of covalent bonds between the crown ether derivatives and the polymer support.

Based on the combined data of elemental analysis and IR spectroscopy, it can be concluded that the immobilization process proceeds with a high degree of efficiency and leads to the formation of chemically bound crown ether groups within the polymer structure. Accordingly, the repeating (elementary) unit of the modified polymer can be represented as a fragment of the styrene–divinylbenzene matrix functionalized with sulfonamide-linked crown ether moieties, where the macrocyclic fragment is covalently attached to the polymer backbone through a spacer group.

Such a structural organization ensures not only the stability of the immobilized active sites but also their accessibility for interaction with substrate molecules and metal cations during catalytic processes.



1а. m=0, n=0, p=0, 2а. m=2, n=0, p=1, 3а. m=6, n=0, p=1,
1б. m=0, n=1, p=0, 2б. m=2, n=1, p=1, 3б. m=6, n=1, p=1,
1в. m=0, n=2, p=0, 2в. m=2, n=2, p=1, 3в. m=6, n=2, p=1.

In order to determine the catalytic activity of synthesized polycrown esters, the nucleophilic substitution reaction of bromine was studied.

$$\text{н-}C_4H_9Br\ (org.) + KI\ (water) \rightarrow \text{н-}C_4H_9I\ (org.) + KBr\ (water)$$

This reaction has previously been used by other researchers to evaluate the effectiveness of crown-containing catalysts.

We examined the influence of the number of immobilized crown ether groups, the presence of a connecting chain (spacer) between the crown ring and the matrix, and the structure of the initial polymer carrier on the yield of n-butyl iodide.

Table 2 — Dependence of the yield of n-butyl iodide on the number of functional groups

Content of crown ether groups in polymer, %	Output, %
-	4.1
7.1	93.3
16.2	99.1
32.4	92.3
50.0	83.1
64.2	77.4
92.0	72.1

An important parameter of catalysts is the number of active groups on the carrier, since catalytic activity depends on the distance between active centers, which, in turn, is determined by the degree of substitution. The table shows that the dependence of the target product yield on the content of crown ether groups in the polymer passes through a maximum.

Discussion. The catalytic activity of modified anion exchangers increases with the degree of substitution up to a maximum value, which corresponds to the presence of 20% active groups in the structure of the carrier, and then gradually decreases. Apparently, a change in polarity in the microenvironment of the active center and a certain degree of interaction between free and complexed cations during the reaction can weaken the activity of the macromolecular catalyst at a high degree of substitution. However, there are examples of the opposite effect of the number of active centers on the efficiency of catalysts, i.e., this parameter requires optimization in each specific case.

It is known that the limiting stage in three-phase catalysis is the diffusion of reagents into and out of polymer granules. Limited diffusion of reagents from the solution to the active groups is one of the main obstacles to the use of polymer catalysts. This disadvantage can be eliminated either by changing the nature of the polymer matrix and its morphology, or by introducing spacer groups between the active center and the polymer backbone. In the catalysts we synthesized, the macrocyclic fragment is connected to the polymer matrix by a hydrocarbon chain of varying length. As expected, the reaction yield increases with increasing length of the connecting chain. Thus, the yield of n-butylium iodide on catalysts 1b, 2b, and 3b is 67.6, 79.4, and 90.1%, respectively.

The speed of reactions carried out under heterophasic conditions strongly depends on both the degree of cross-linking and the morphology of macromolecules.

The effect of the degree of swelling was studied on catalysts based on AN-22 anionite (Table 3).

Table 3 — Effect of crosslinking degree copolymer of styrene and divinylbenzene

Content crown ether, %	DVW content, mol. %	Output, %
Catalyst 2v		
20	1	89,4
	2	83,1
	4	65,7
	8	58,4
	12	54,6

10	1	82,1
	2	64,5
Catalyst 2v		
20	1	89,1

The table shows that as the amount of DVB in the anionite increases, the activity of the catalyst decreases sharply.

The observed trend may also be caused by different diffusion rates of reagents in the catalyst grain, associated with an increase in the density of cross-links in the macromolecule and, accordingly, a decrease in the swellability of the polymer.

The influence of the morphology of the initial anion exchangers was studied on catalysts obtained by immobilizing CSB15C5 on AN-21 gel, macroporous, and macromolecular structures with a 1% cross-linking agent content (see Fig.). The figure shows that the catalysts studied are ranked in the following order in terms of activity: macro-mesh > macroporous > gel. The higher activity observed when using macro-mesh anion exchangers (divinylbiphenyl instead of divinylbenzene) is due to the presence of larger pores in the polymer mesh.

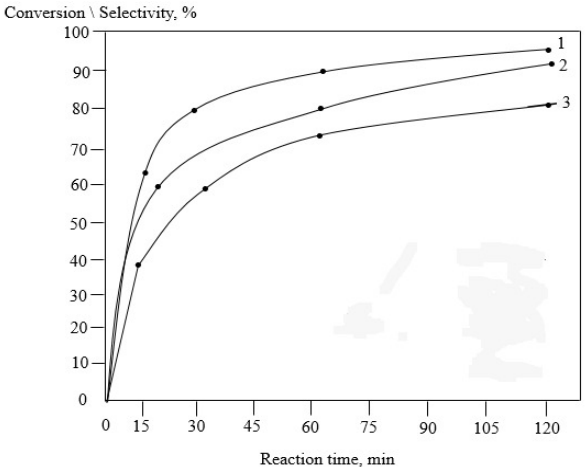


Figure 1 — Kinetic conversion curves of n-butyloxide in the presence of catalysts macro-mesh (1), macroporous (2) and gel (3) structures

The catalytic effect also depends on the nature of the salt cation used in the nucleophilic substitution reaction in n-butyl bromide. The data in Table 4 show that when crown-containing catalysts are used, the principle of matching the crown ring cavity to the diameter of the salt cation is preserved.

Table 4 — Dependence of the catalytic activity of catalysts on the content of natural salts

Salt	Catalyst	Output, %
Catalyst 2v		
KI	3в	99,1

NaI	3в	96,4
KI	3б	97,6
NaI	3б	94,6
KI	3а	51,4
NaI	3а	56,2

The results obtained in this work show that the activity of immobilized crown ether catalysts depends on many factors, among which the most important are the number of crown ether groups, the composition and structure of the polymer matrix, which determines the swelling of the carrier and the accessibility of active centers.

The mechanism of action of an interphase catalyst can be represented as follows:

$$P—CE•MУ+RX \rightarrow P—CE•MX+RУ \text{ (organic phase);}$$
$$У^- + M + X^- \text{ (aqueous phase).}$$

When the interphase transfer catalyst is insoluble in both the organic and aqueous phases, the interphase transfer catalyst will be present in the third phase, so that both reactants are transferred to the third phase, where the two reactants are dissolved in each other and the concentration is very high, which can show high reactivity, so that the reaction rate is obviously improved.

The reaction should occur in the organic phase around the catalytic center. Anions are exchanged at the water-organic phase interface with inorganic K+ cations and cations on the P-KE polymer carrier in the aqueous and organic phases, respectively. Thanks to the presence of a phase transfer catalyst, the negative ions involved in the reaction have high reactivity, and the process is simplified.

Conclusion. In this work, crown ether derivatives were successfully immobilized onto polymeric anion exchangers with different structural characteristics, resulting in the formation of efficient polymer-supported interphase transfer catalysts. The obtained materials combine the high complexing ability of crown ethers with the advantages of heterogeneous systems, including stability, reusability, and ease of separation. It was demonstrated that the catalytic activity of the synthesized systems strongly depends on several key factors, including the structure and morphology of the polymer carrier, the degree of crosslinking, the swelling ability of the matrix, and the content and spatial accessibility of crown ether groups. In particular, macroreticular and macroporous supports обеспечивают higher catalytic efficiency due to improved diffusion of reagents and better accessibility of active centers.

The results of catalytic testing in nucleophilic substitution reactions confirmed that polymer-supported crown ether catalysts exhibit high activity and selectivity under interphase conditions. At the same time, an optimal concentration of active groups was identified, at which maximum catalytic efficiency is achieved, indicating the importance of balancing functionalization degree and microenvironment polarity. A significant advantage of the developed catalysts is their heterogeneous nature. Being insoluble in aqueous and organic media, they can be easily separated from the reaction mixture by simple filtration and reused multiple times without significant loss of activity. This

makes them particularly attractive for practical applications, including continuous-flow processes and industrial-scale synthesis. In addition, the use of such catalysts contributes to the development of environmentally friendly chemical technologies, as they reduce the need for hazardous reagents, minimize waste generation, and allow the use of milder reaction conditions.

Thus, polymer-supported crown ether catalysts represent a promising class of interphase transfer catalysts with high potential for application in organic synthesis and industrial processes. Further research should focus on optimizing the structure of polymer matrices, improving mass transfer characteristics, and expanding the range of catalytic reactions in order to fully realize their practical potential.

References

Benaglia M., Puglisi A. Cozzi F. (2003) Polymer-Supported Organic Catalysts. Chem. Rev. 103:3401–3429. (in English)

Cozzi F. (2006) Immobilization of organic catalysts. When, why, and how. Adv. Synth. Catal. 348:1367–1390. (in English)

Demlov E., Demlov Z. (1987) Mezhfaznyj kataliz [Interphase Catalysis]. Moscow. — 488 p. (in Russian)

Dong S., Gao L., Chen J., Yu G., Zheng B., & Huang F. (2013). A supramolecular polymer formed by the combination of crown ether-based and charge-transfer molecular recognition. Polymer Chemistry, 4(4):882-886. (in English)

Duan Z., Xu F., Huang X., Qian Y., Li H., & Tian W. (2022). Crown Ether-Based Supramolecular Polymers: From Synthesis to Self-Assembly. Macromolecular Rapid Communications, 43(14):2100775. (in English)

Ergozhin E.E., Kurmanaliev M.K. (1994) Polimery na osnove kraun-soedinenij [Polymers based on crown compounds]. – Almaty: Gylym. — 272 p. (in Russian)

Ergozhin E.E., Kurmanaliev M.K. (1995) Polikraunefiry, problemy i perspektivy [Polycrown ethers, problems and prospects]. Proceedings of the National Academy of Sciences of Kazakhstan. Chemistry series. 1:4-257. (in Russian)

Ergozhin E.E., Kurmanaliev M.K. (2020) Osnovy ionoobmena [Fundamentals of Ion Exchange]. – Almaty, Almanac. — 275 p. (in Russian)

Ergozhin E.E., Kurmanaliev M.K., Idrisova K.S. (1991) Sintez i issledovanie svojstv kraunsoderzhashchih polisul'fonamidov [Synthesis and study of the properties of crown-containing polysulfonamides]. Reports of the USSR Academy of Sciences. 320:6. — P.1389-1391. (in Russian)

Ford W. T., Tomoi M. I. (1984) Advances in Polymer Science. Berlin, 1984. 55:50-104. (in English)

Hashimoto T., Maruoka K. (2007). Recent development and application of chiral phase-transfer catalysts. Chemical Reviews, 107(12):5656-5682. (in English)

Huang F., Scherman O. A. (2012). Supramolecular polymers. Chemical Society Reviews, 41(18):5879-5880. (in English)

Lu, J., Toy P.H. (2009) Organic Polymer Supports for Synthesis and for Reagent and Catalyst Immobilization. Chem. Rev. 109: 815–838. (in English)

Mąkosza M., Fedoryński M. (2003). Phase transfer catalysis. Catalysis reviews. 45(3-4):321-367. (in English)

Makosza M., Fedorynski M. Interfacial Processes. (2020) The Key Steps of Phase Transfer Catalyzed Reactions. Catalysts. 10:1436 (in English)

Ooi T., Maruoka K. (2007). Recent advances in asymmetric phase-transfer catalysis. Angewandte Chemie International Edition, 46 (23):4222-4266. (in English)

Rosaria Schettini, Maria Rosaria Acocella. (2024) State Of The Art Of Supported Phase Transfer-Catalysts Onium Salt-Based. ChemCatChem. 16:1-14. (in English)

Shuangshuang Liu and Weihao Zhu. A (2022) Minireview of Phase-Transfer Catalysis and Recent Trends. Biomed J Sci & Tech Res 45(4). BJSTR. MS.ID.007237. (in English)

Siewniak A., Monasterska E., Pankalla E., Chrobok A. (2022) Polymer-Supported Poly (Ethylene Glycol) as a Phase-Transfer Catalyst for Cross-Aldol Condensation of Isobutyroaldehyde and Formaldehyde. Molecules. 27:6459. (in English)

Starks C. M., Halper M. (2012). Phase-transfer catalysis: fundamentals, applications, and industrial perspectives. Springer Science & Business Media. (in English)

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