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Membrane assisted liquid phase catalytic oxidation of sulfides

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Abstract

A reverse osmosis/nanofiltration technique was applied to recover the soluble catalyst —sodium salt of tetra(sulfophthalocyanine)-cobalt(II) —from the reaction solutions in the liquid phase oxidation of sodium sulfide. Conditions for the efficient recovery of the catalyst were determined. A catalyst recovered by reverse osmosis/nanofiltration retains its activity and selectivity, and can be re-used in the reaction. A catalytic membrane was prepared by adsorption of the Co-TSPC catalyst over a porous membrane. Advantages of using the membrane as a catalyst support were demonstrated.

1. Introduction

Catalytic reactions combined with various methods of separation form the basis for technologies in chemistry and related industries. Traditionally, these stages were being investigated and developed independently, until the pioneering findings of membrane catalysis [1,2] have demonstrated the promising potentials of their integration.

At present, membrane methods are mostly employed in the processes based on enzymatic and heterogeneous catalysis [3–8]. Prospects of these techniques applied to the homogeneous liquid phase catalysis have been far less studied [9–11]. Meanwhile, one of the traditional problems in homogeneous catalytic processes is that of a separation, namely separation of the catalysts and reaction solutions. Membrane methods may provide a new means for solving this problem.

Our work was focused at the investigations of membrane methods applied to the homogeneous catalyst recovery in the process of liquid phase catalytic oxidative detoxication of sulfides and mercaptanes, which are produced in large quantities by various natural and industrial sources. Both economical and environmental considerations imply that in this process, oriented at the environment protection, the catalyst loss with the treated effluent stream should be avoided. From this standpoint, potentials of reverse osmosis and nanofiltration in the catalyst recovery from the reaction solutions, as well as those of its binding to a porous membrane were studied.

2. Experimental

2.1. Reaction

The reaction under consideration

$$S^{2-} + n\,O_2 \rightarrow S, SO_3^{2-}, S_2O_3^{2-}, SO_4^{2-}$$

occurs in aqueous solutions at ambient temperature and a pH range of ca. 7–13. It is catalyzed by the sodium salt of tetra(sulfophthalocyanine)-

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cobalt(II), briefly Co-TSPC, dissolved in the solutions being treated. Co-TSPC is the highly active catalyst; a pronounced acceleration of the reaction rate was registered at its concentrations as low as $1\text{–}2 \cdot 10^{-9}$ M [12]. In this study, Co-TSPC manufactured at Novosibirsk Bureau of Catalysts 'SKTB Katalizator' and purified as described in [13] was used.

The reaction selectivity is principally determined by the pH value of the solution; at pH close to 7, sulfur was the main product, while oxygen-containing compounds were typically produced at high pH. In order to maintain the desired pH during the reaction, potassium phosphate buffer was added to the solution according to [14].

2.2. Analysis

The reaction performance was monitored by means of the chemical analysis of sulfur-containing compounds [12], spectrophotometric analysis of Co-TSPC catalyst [15] and measurements of the pH of the solutions.

2.3. Setup

Catalytic runs were carried out in the glass apparatus with the thoroughly stirred batch-type reactor described in details elsewhere [12,16]. Reverse osmosis/nanofiltration separations of the solutions were performed at ambient temperature under the pressure of pure argon in the stainless steel stirred cell [17]. Polyamide thin film composite reverse osmosis membranes OPM-K, OPAM-K (operating pressure 3 MPa) and poly(vinyl alcohol) thin film composite nanofiltration membrane OPMN-K (operating pressure 1.5 MPa), manufactured by Research and Manufacturing Association NPO Polimersintez (Vladimir, Russian Federation) [18], were used. For the adsorption of Co-TSPC catalyst, a variety of ultra-and microfiltration membranes were tested as supports.

2.4. Reagents

Na_2S (technical grade) was purified before use by means of recrystallization from the aqueous solution. Phosphate buffer, used to stabilize the pH of the reaction solution, was prepared by adding the adequate amount of KOH solution to ortho-phosphoric acid; the reagents used were of 'chemically pure' grade, according to Russian standards. Compressed oxygen from a cylinder with the purity 99.4% was used without purification.

3. Results and discussion

The catalytic runs were carried out within the whole range of pH where the reaction is known to occur (pH 7–13). Table 1 shows conditions and results of the typical runs. As can be seen, with the fresh catalyst samples (runs 1 and 3) virtually complete conversions of sodium sulfide were achieved, the reaction products being sulfur and thiosulfate anion.

When the reaction was brought to completion, sulfur was filtered out from the reaction mixtures,

Table 1
Homogeneous oxidation of Na_2S with the membrane recovery of Co-TSPC catalyst

Run no.	Conversion of S^{2-} (%)	Yield (%)		Catalyst activity (mol $O_2 \cdot$ Co-TSPC$^{-1} \cdot$ min^{-1})
		S	$S_2O_3^{2-}$	
1	100	69	31	$1 \cdot 10^3$
2	100	54	46	$1.3 \cdot 10^3$
3	100	80	20	$0.6 \cdot 10^3$
4	98	60	38	$0.5 \cdot 10^3$

Reaction conditions: $T = 298$ K, $P_{O_2} = 0.1$ Mpa, $C_{Na_2S} = 0.05$ M, $C_{H_2PO_4^-} = 0.5$ M.

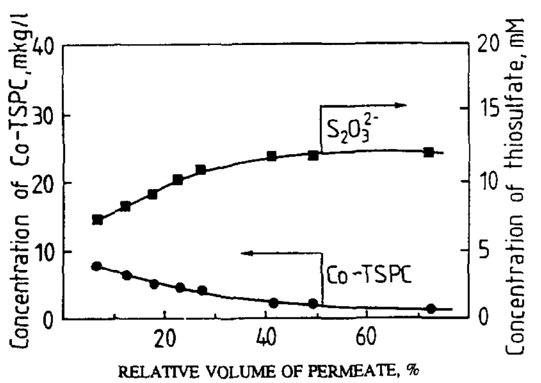

Fig. 1. Concentrations of Co-TSPC catalyst and $S_2O_3^{2-}$ product upon RO separation of the reaction solution. Operating conditions: membrane OPM-K, temperature 298 K, pressure 3 MPa.

and reverse osmosis (RO) or nanofiltration (NF) separation of the remaining solutions were performed. Permeates containing very low concentrations of the catalyst and appreciable concentrations of thiosulfate were obtained (Fig. 1). The retention values calculated from these data (Fig. 2) were very high for the catalyst —often in excess of 99.9 —which agrees well with the results obtained with the mono-component Co-TSPC solutions. Meanwhile, the retention of the thiosulfate anion was found to be around 50%, which is lower than that for the mono-component solutions of sodium thiosulfate (up to 95–99%, particular values being determined by the separation conditions). The reasons causing this discrepancy will be discussed below.

With the obtained retentates as catalysts, the comparative catalytic runs were carried out. The results summarized in Table 1 (runs 2 and 4) clearly show that the activities and selectivities of the recovered catalysts remain essentially the same as those for the fresh samples. In agreement with this conclusion, identical UV-spectra have been revealed for the fresh Co-TSPC catalysts and the ones recovered by reverse osmosis or nanofiltration.

Thus, for the reaction between sulfide anion and dioxygen, catalyzed by the sodium salt of tetra(sulfophthalocyanine)-cobalt(II), the efficient recovery of the catalyst from the reaction solutions can be achieved through the use of reverse osmosis/nanofiltration techniques.

3.1. Negative retention of thiosulfate anion

As mentioned above, the retention values for thiosulfate anion registered during reverse osmosis or nanofiltration separations of the reaction solutions were markedly lower than those found for the 'model' sodium thiosulfate aqueous solutions of equal concentrations. Note that the similar phenomenon has been previously observed in [15,19] during the reverse osmosis separation of mixed solutions containing sodium nitrate and sodium salts of various heteropoly acids. It was shown that the retention of the nitrate anion was strongly affected by the highly retained heteropoly anions, decreasing down to the negative values as the concentration of the latter became high enough.

We believe that the phenomenon of negative retention, if properly handled, can be applied to solve some separation problems. In the present case, one may expect high separation of the catalyst and soluble sulfur-containing products to be achieved due to the negative retention of the latter. In view of the possible applications, nanofiltration of the reaction solutions was investigated in more details.

Upon nanofiltration of sodium thiosulfate aqueous solutions (concentrations 0.001–0.01 M, pH = 7–9, operating pressure 1.5 MPa, $t = 20°C$) it was found that the $S_2O_3^{2-}$ anion retention equals to 95–99%. Besides, $S_2O_3^{2-}$ retention did not depend on the Co-TSPC catalyst concentration within $1 \cdot 10^{-9}$–$1 \cdot 10^{-5}$ M limits, though it was definitely dependent on the phosphate buffer con-

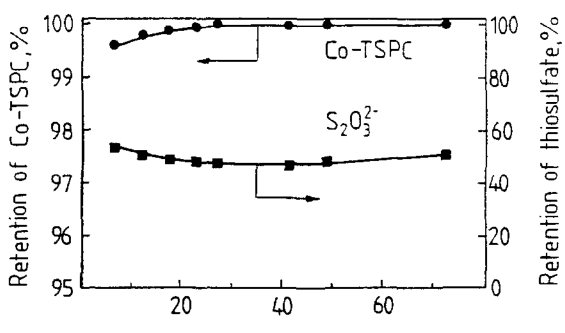

Fig. 2. Retentions of Co-TSPC catalyst and $S_2O_3^{2-}$ product upon RO separation of the reaction solution. Operating conditions: see Fig. 1.

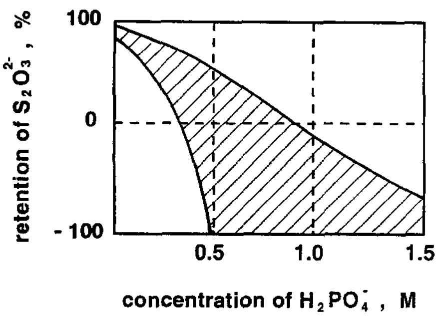

Fig. 3. Retention of $S_2O_3^{2-}$ anion vs. concentration of $H_2PO_4^-$ co-ion upon nanofiltration of the mixed solutions of $Na_2S_2O_3$ and the phosphate buffer. Operating conditions: membrane OPMN-K, temperature 298 K, pressure 1.5 MPa.

centration. As seen from Fig. 3, an increase of the buffer concentration gives rise to a continuous decrease of thiosulfate retention down to the negative values, which are attained at $H_2PO_4^-$ concentrations exceeding 0.5 M. Retention of $H_2PO_4^-$ remains high, being equal to that for the mono-component solutions of equal concentrations.

The observed dependence of retention upon co-ion concentration is apparently caused by the difference in membrane permeabilities to the different ions in the mixed solutions of electrolytes. At appreciable concentrations of a well-retained ('slow') anion, low retention of the second ('fast') co-ion becomes necessary to maintain electroneutrality of the permeate flux. Detailed analysis of the mechanism of negative retention can be found elsewhere [20–24].

3.2. Catalysis by the membrane-bound Co-TSPC

In response to the need for the efficient means of catalyst separation in the liquid phase reactions, catalysis by the anchored metal complexes has been developed during the last decades [19,25–28]. This new approach had been much inspired by the idea to combine the merits of homogeneous and heterogeneous catalysts. Perhaps the main problem in this field is to prepare the support-bound (i.e. heterogenized) catalysts which would possess the same catalytic properties as their homogeneous analogs. An abundant experience of a number of researches evidences though that the anchoring, and more generally the heterogenization of homogeneous catalysts, often results in a substantial decrease of the catalytic performance. These changes are normally being assigned to the chemical and/or structural transformations of catalysts due to the heterogenization. Meanwhile, changes of the mass transfer conditions which inevitably result from a catalyst binding to a grained porous support may likewise provoke the activity decrease. The results reported below apparently confirm this point.

For the reactions catalyzed by Co-TSPC, the problem of the catalyst heterogenization is not solved yet. In the search for an appropriate support for the catalyst, the porous membrane was found capable to adsorb Co-TSPC in appreciable concentrations. Two samples containing Co-TSPC adsorbed over the membrane and differing in the membrane size and the catalyst content were tested for the catalytic performance in the same experimental conditions that were previously employed for the homogeneous catalytic runs. The samples were cut into pieces of ca. 3 × 3 mm and dispersed in the thoroughly stirred reaction solutions. Some characteristics of the membrane-bound catalyst samples and results of the catalytic runs are summarized in Table 2. The non-catalytic experiment (run No. 1) has been carried out for comparison.

For the both samples the Co-TSPC concentration at the membrane surface, calculated at the assumption of the uniform covering, was within a monolayer. For the M-1 sample, the average surface concentration of Co-TSPC was 50-fold greater than that for the M-2 one. As can be seen, no catalytic activity was registered for the M-1 membrane (compare the results of runs 3 and 1), while for the M-2 the activity was clearly observed.

Two reasons for the activity decrease of the Co-TSPC fixed to the membrane were considered: (1) the catalyst deactivation upon adsorption onto the membrane, and (2) diffusion of the reactants within the pores of the membrane.

Table 2
Rate of Na_2S oxidation in presence of homogeneous and membrane-bound Co-TSPC catalyst

Run no.	Amount of Co-TSPC (mg)	Reaction rate ($mol\ O_2 \cdot l^{-1} \cdot s^{-1}$)	Effectiveness factor
Homogeneous:			
1	0	$2 \cdot 10^{-5}$	–
2	0.5	$16 \cdot 10^{-5}$	–
Membrane-bound:			
3	0.5 (M-1)[a]	$2 \cdot 10^{-5}$	0
4	1.0 (M-2)[b]	$6 \cdot 10^{-5}$	0.2

Reaction conditions: $T = 298$ K, $P_{O_2} = 0.1$ MPa, $C_{Na_2S} = 0.05$ M, pH = 7–8. Characteristics of the membrane: surface area 24 m^2 /g, thickness 0.1 mm, density 0.41 g/cm^3

[a] External surface of the M-1 membrane sample $6 \cdot 10^{-4} m^2$.

[b] External surface of the M-2 membrane sample $6 \cdot 10^{-2} m^2$.

The catalyst deactivation upon adsorption is unlikely to take place, as UV-VIS spectra of the membrane-bound Co-TSPC catalyst were identical to those of the homogeneous one described in [15]. On the other hand, the reactants diffusion within the pores of the membrane seems to play an important role in this case of the highly active catalyst. Apparently, it is due to the diffusion that the catalytic reaction was not observed with the M-1 membrane of the high surface concentration of the catalyst, while it became noticeable as soon as the catalyst concentration was decreased in the M-2 membrane. This assumption is supported by the calculations of the Thiele modulus which is being used to evaluate the diffusion influence at the reaction performance [29]. The above mentioned decrease of the surface concentration of Co-TSPC catalyst results in the corresponding decrease of the effective reaction rate constant and hence of the Thiele modulus. In turn, this means that the reaction over the M-2 sample is less affected by the diffusion then the one occurring over the M-1.

The evaluations of the Thiele modulus are in accordance with the observed performance of the membrane-bound catalyst samples. The reaction rates, measured with the homogeneous Co-TSPC catalyst (R_{hom}) and the one adsorbed over the membranes (R_{ads}), and compared according to the equation $E = R_{ads}/R_{hom}$ [29], gave rise to the effectiveness factor $E = 0$ for the M-1 and $E =$ ca. 0.2 for the M-2 membranes.

These results support the assumption that the reaction catalyzed by the membrane-bound Co-TSPC is influenced by the reactants diffusion in the pores of the membrane. Moreover, they indicate that the homogeneous Co-TSPC catalyst apparently can not be fixed to the surface of typical grained porous supports without a substantial decrease of the catalytic activity caused by the internal diffusion. On the other hand, a porous membrane when used as the catalyst support may provide a key to the solution of the diffusion problem. A forced flow of the reacting liquid mixture through the uniform pores of the membrane instead of a slow diffusion of reactants in the pores of a typical grained support may improve the conditions for the reactants transport to and from the catalytic surface.

A validity of the latter assumption has been verified experimentally. For that, new samples of the membrane-bound Co-TSPC were prepared and tested in the stirred membrane reactor with Na_2S solution flowing through the membrane under oxygen pressure. Permeates and retentates (i.e., the portions of the solution that had passed through the membrane and had not passed, respectively) were analysed for the content of sulfur-containing compounds and Co-TSPC. The experimental results are shown in Table 3.

Although no Co-TSPC was found in the permeates and non-permeates, an appreciable catalytic conversion of sulfide was detected in the permeates (in the retentates, the conversion of

Table 3
Na_2S oxidation catalyzed by the membrane-bound Co-TSPC (flow regime)

Catalytic membrane	Sample analyzed	Conversion of S^{2-}	Contact time minutes
1	Retentate	14.7	5
1	Permeate	52.7	
2	Retentate	27.4	11
2	Permeate	50.3	

Reaction conditions: $T=298K$, $P_{O_2}=0.115$ MPa, $C_{Na_2S}=0.04$ M, pH = 13, amount of Co-TSPC: 1.7 mg, external surface of the membrane $1.1\cdot10^{-2}m^2$.

S_2^- was due to the non-catalytic oxidation). These data confirm the above assumption that the reaction is strongly affected by the reactants diffusion in the pores of a supporting material; besides, our expectation to influence the diffusion by means of a forced flow of the reaction solution through the porous catalytic membrane appears to be fulfilled.

4. Conclusions

Reverse osmosis/nanofiltration technique was applied to recover the soluble catalyst —sodium salt of tetra(sulfophthalocyanine)-cobalt(II) — from the reaction solutions in the liquid phase oxidation of sodium sulfide. Conditions for the efficient recovery of the catalyst were determined. A catalyst recovered by reverse osmosis/nanofiltration retains its activity and selectivity, and can be re-used in the reaction.

A catalytic membrane was prepared by adsorption of the Co-TSPC catalyst over a porous membrane. Advantages of using the membrane as a catalyst support were demonstrated.

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