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Preparation, characterization, and catalytic activity of synthetic carbon-supported (phthalocyaninato)cobalt-containing complexes in dodecane-1-thiol oxidation reaction

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Abstract

Several heterogeneous catalysts consisting of peripherally substituted cobalt phthalocyanine complexes covalently linked to the synthetic carbons modified by organic aminogroups have been prepared and tested in the catalytic reaction of the autoxidation of dodecane-1-thiol in organic solvents. It has been shown that, in general, the catalytic activity of covalently linked cobalt phthalocyanine sulfonamides is higher as compared to the respective cobalt phthalocyanine sulfonic acids. An influence of the length of the linker and surface concentration of the phthalocyanine complexes on the catalytic activity of a given catalyst has also been discussed.
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1. Introduction

Transition-metal phthalocyanines (Fig. 1) have been widely used as catalysts for the variety of organic transformations [1–3]. Selective oxidation of various organic thiols into the respective disulfides is the key reaction in the Merox process [4] (Scheme 1), which is, in particular, very important for the preparation of the high quality jet fuels. Among the numerous tested catalytic systems, peripherally substituted as well as unsubstituted cobalt phthalocyanine complexes are, probably, the best known catalysts for this reaction [4,5]. The immobilization of cobalt phthalocyanine complexes on various inorganic and organic supports affords the preparation of technologically useful catalysts [1,4,6–8]. The immobilization of transition-metal phthalocyanine complexes can be achieved by a number of methods including physical adsorption of metallocomplexes on zeolites [8,9], inorganic oxides [10,11], aluminum oxide [12], silica

gels [13], and activated carbons [14–16]. The physical adsorption approach, however, leads to the continuous depression of the catalytic activity because of the appreciable desorption and removal of transition-metal phthalocyanines during the time course. Covalent anchoring of peripherally substituted cobalt phthalocyanines onto the surface of modified silica gels [17] or organic polymers [26] is another method for the preparation of heterogeneous catalysts useful for the Merox process. It is commonly believed that the key difference between physical adsorption and covalent anchoring methods is the formation of a multilayer structure with strong intermolecular interactions in the former case and the formation of the monomeric structure, at least theoretically, in the later case (Scheme 2) [14]. The degree of aggregation, in turn, can control the activity of the respective catalyst but there is no general agreement on the relationship between the aggregation state of substituted cobalt phthalocyanines and their catalytic activity [18–21].

The optimal conditions for the transformation of the organic thiols into the respective disulfides require the presence of the base either in solution or on the surface of a heterogeneous catalyst. Thus, the influence of the nature and type of the surface

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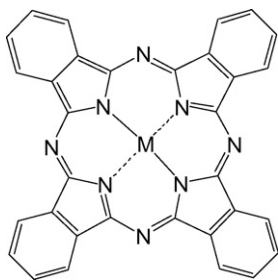*E-mail address:* vnemykin@d.umn.edu (V.N. Nemykin).

Fig. 1. Structure of transition-metal phthalocyanine core.

groups on modified activated carbon or silica gel supports on the catalytic activity of immobilized phthalocyanine complexes have been briefly discussed in the literature [14]. In general, immobilization of the basic groups on the surface of a heterogeneous catalyst yields more technologically compatible systems. However, influence of the structure of surface-anchored basic groups on the activity of substituted cobalt phthalocyanines in the Merox process has never been targeted.

In the present work, we present the preparation, characterization, and preliminary data on the catalytic activity of sulfonated cobalt phthalocyanine complexes covalently anchored on the surface of a modified activated carbon. The influence of the carbon surface and topology of surface groups on the catalytic activity of cobalt phthalocyanine is also discussed.

2. Experimental

2.1. Physical methods

Surface area of the different carbons has been determined by the standard adsorption–desorption isotherms [22] with helium and argon gases using ASAP-2010C surface analyzer. UV–vis spectra were recorded using Hewlett-Packard 8453 and Specord-M40 spectrometers in the 260–900 nm range in water and DMF as the solvents. The distribution of acidic functional groups on the surface of the oxidized carbons was analyzed by Boehm's method [23]. In this approach, the total number of the exchangeable protons was determined using sodium hydroxide titration, while the concentration of carboxylic groups on the surface was calculated on the basis of the titration experiments with sodium carbonate. In both cases, the samples of carbon have been equi-

$$2RSH \xrightarrow{O_2} RSSR + H_2O_2$$
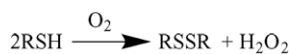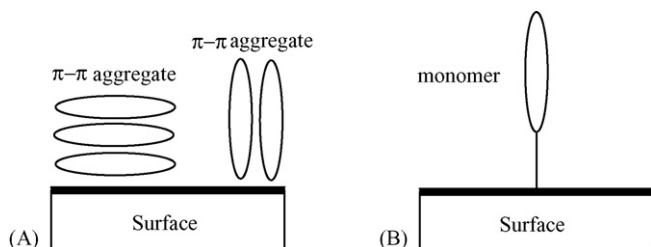
Scheme 1.

Scheme 2.

librated with an excess of a respective base for 72 h at $22 \pm 2\,^{\circ}C$ using an orbital shaker. The equilibrated solutions were filtered to remove the activated carbon and then the aliquots were titrated by standardized hydrochloric acid using methyl-red as the indicator. The determination of surface aminogroups was conducted by equilibration of the samples with an excess of hydrochloric acid for 72 h at $22 \pm 2\,^{\circ}C$ followed by the titration of the aliquots using a normalized sodium hydroxide solution. All titration experiments were performed in triplicate and the statistical variance was found not to exceed five percent.

2.2. Preparation of the catalysts

Cobalt 4,4′,4″,4‴-tetrasulfophthalocyanine, $CoPc^{(SO_3H)_4}$, and cobalt 4,4′,4″,4‴-phthalocyaninetetrasulfonyl chloride, $CoPc^{(SO_2Cl)_4}$, were prepared as described in literature [24]. The starting activated carbon used in this paper was SKN (the surface area 1200–1300 m^2/g), which has been prepared from the porous spherically granulated vinylpyridine–divinylbenzene copolymer and activated using standard methods described in literature [22].

2.2.1. Preparation of SKN-Ox

The oxidation of the SKN samples was conducted by refluxing of respective carbon with 25% nitric acid for 15 h (the oxidant was replaced every 4 h). Humic-type compounds formed during the oxidation process were eliminated by washing the resulted carbons (designated as SKN-Ox) with distilled water followed by the treatment with hot 1% sodium hydroxide solution until colorless filtrates and finally with distilled water until pH 9. Recovering of the acidic form of SKN-Ox samples has been accomplished by the treatment of a respective carbon with a 5% solution of hydrochloric acid followed by a final wash with distilled water. The resulted carbons were dried overnight at 105 °C, cooled down to room temperature, and then stored under a dry air atmosphere. Prepared by this method the SKN-Ox carbon has the surface area of 907 m^2/g, the concentration of carboxylic groups of 1.9 meq/g, and the concentration of phenolic groups of 0.9 meq/g.

2.2.2. Preparation of SKN-Cl

In the next step, the surface carboxylic groups in the SKN-Ox carbon have been transformed into the corresponding chloroanhydrides by the refluxing of the respective carbons for 12 h with the 1000-fold excess of thionyl chloride in dry degassed benzene followed a wash with dry benzene. The resulting carbon (designated as SKN-Cl) has been dried in vacuum and used as freshly prepared material in the next step.

2.2.3. Preparation of SKN-n

The covalent anchoring of the organic diamines of general formula of $H_2N–(CH_2)_n–NH_2$ ($n = 3$, 4, 5, and 7) has been achieved by the refluxing of the freshly prepared samples of SKN-Cl with a three-fold excess of the respective amine and three-fold excess of pyridine in dry benzene for 8 h. The resulting product (designated as SKN-n, $n = 3$, 4, 5, and 7) has been filtered, dried in vacuum, washed with 1% aqueous sodium

hydroxide and finally several times with distilled water. In each case the samples were equilibrated for 12 h in order to remove all traces of sodium hydroxide from the carbon surface.

2.2.4. Preparation of SKN-n-H and SKN-n-N

Two different procedures were used for the preparation of the heterogeneous cobalt phthalocyanine-containing catalysts. In the case of immobilization of $CoPc^{(SO_3H)_4}$ complex, the sample of respective SKN-*n* carbon (1.5 g) and 50 ml of 1×10^{-4} mol/l solution of $CoPc^{(SO_3H)_4}$ in water (50 ml) were stirred at room temperature for 4 h. Then the catalyst was filtered, transferred into distilled water for 12 h, filtered again, washed several times with distilled water and dried at room temperature. The catalysts prepared using this method were designated as SKN-*n*-H (*n* = 3, 4, 5, and 7). In the case of immobilization of $CoPc^{(SO_2Cl)_4}$, a sample of the respective SKN-*n* carbon (1.5 g) was stirred with 1×10^{-4} mol/l solution of $CoPc^{(SO_2Cl)_4}$ and 0.1 ml of pyridine in 50 ml of extra dry DMF at 60 °C for 48 h. After this period of time, a large excess (0.5 g) of *N,N*-dimethylethylenediamine was added and the reaction mixture was stirred for another 24 h at 60 °C. The resulting catalyst was filtered, transferred into distilled water for 24 h, and filtered again. This operation was repeated several times in order to eliminate all unreacted *N,N*-dimethylethylenediamine. Finally, the catalyst was filtered, washed several times with distilled water and dried at room temperature. The catalysts prepared using this method were designated as SKN-*n*-N. In both approaches, the amount of the adsorbed substituted cobalt phthalocyanine was calculated as the difference between the initial amount of a macrocycle and that of the phthalocyanine complex recovered in filtrates using UV–vis spectrophotometry.

2.3. Evaluation of catalytic properties

The autoxidation of dodecane-1-thiol in octane solution has been selected as the test reaction to probe the catalytic activity of new heterogeneous catalysts (i.e. viewing their potential application in the Merox process). Oxidation reactions were conducted under ambient air pressure at 50 °C for 30 min with vigorous stirring unless specifically mentioned in the text. In all cases, 100.0 mg of a respective catalyst has been mixed with 10.0 ml of 0.0538 M solution of dodecane-1-thiol in octane. The final concentration of the thiol was monitored using potentiometric titration with a precision of ±5% and found to be consistent (within ±5%) with the concentration of formed disulfide monitored by GC–MS (conducted for SKN-5-H and SKN-5-N systems). It was found that the catalytic activity of the SCN-5 support is negligibly small (<7%) as compared to that found in phthalocyanine-containing catalysts. In the catalyst poisoning experiments, the respective catalyst was filtered after each cycle, washed with octane, and dried before the next catalytic experiment. In all cases, the mass of a dry catalyst was found to be a constant (±0.5 mg). Finally, in all base-regeneration reactions, the respective catalysts first were filtered, washed with octane, and dried. After this, each catalyst has been washed three times with 5 ml of 0.05% aqueous solution of sodium hydroxide, then with deionized water, and dried prior the next catalytic cycle.

3. Results and discussion

3.1. Preparation and characterization of catalysts

The ideal bifunctional heterogeneous catalyst for the Merox process should combine a catalytically active transition-metal center with a high dioxygenase activity and basic groups on the surface of the catalyst [4,25]. In order to satisfy both of these conditions, several approaches have been suggested in the literature including the physical adsorption of cobalt phthalocyanine on the surface of a basic inorganic support or covalently linking the phthalocyanines to the surface of aminosilica gel or aminated organic polymers [25,26]. Here we used a new synthetic approach for the preparation of a basic carbon surface, which is able to covalently link substituted cobalt phthalocyanines. Oxidation of the starting basic (pyridine-containing) activated carbon by diluted nitric acid leads to the formation of carboxylic groups on the carbon surface along with phenol and lactone functional groups [22]. Out of these, carboxylic groups can be transformed into chloroanhydrides by the reaction with thionyl chloride (Fig. 2). The reaction of the chloroanhydride groups on the surface of activated carbon with different diamines of general formula $H_2N(CH_2)_nNH_2$ leads to the formation of target modified carbons with basic surface groups. It is interesting to note that the concentration of surface aminogroups is nearly constant for the SKN-*n* (*n* = 3–5) carbons, while it is significantly smaller in the case of SKN-7 carbon. As a result, in SKN-*n* (*n* = 3–5) carbons almost all surface carboxylic groups were transformed into sulfonamides, while only 62% of those were modified in the case of SKN-7 carbon (Table 1). The resulting surface area of SKN-*n* carbons is also organic amine dependable but no general trend has been observed. Cobalt 4,4′,4″,4‴-tetrasulfophthalocyanine and cobalt 4,4′,4″,4‴-phthalocyaninetetrasulfonyl chloride have been immobilized on the surface of SKN-*n* carbons by the formation of covalent amide bonds. The number of basic functional groups in the heterogenic catalyst can be increased by the transformation of the additional sulfonyl chloride substituents into *N,N*-dimethylethylsulfonamide groups by the reaction between immobilized cobalt 4,4′,4″,4‴-phthalocyaninetetrasulfonyl chloride and *N,N*-dimethylethylenediamine (Fig. 2). Based on the titration experiments, not all of the surface aminogroups have been used for the covalent linking of cobalt phthalocyanines in spite of the large excess of phthalocyanines used. The concentration of the survived aminogroups increases with the increase of the length of used amines (Table 1). As a

Table 1
Selected characteristics of the modified activated carbons

Carbon	C_{NH_2} (meq/g)[a]	C_{CO_2Na} (%)[b]	Surface area
SKN-3	1.572	17.3	591.5
SKN-4	1.572	17.3	791
SKN-5	1.621	14.7	774.5
SKN-7	1.18	37.9	420

[a] Concentration of aminogroups on the surface.
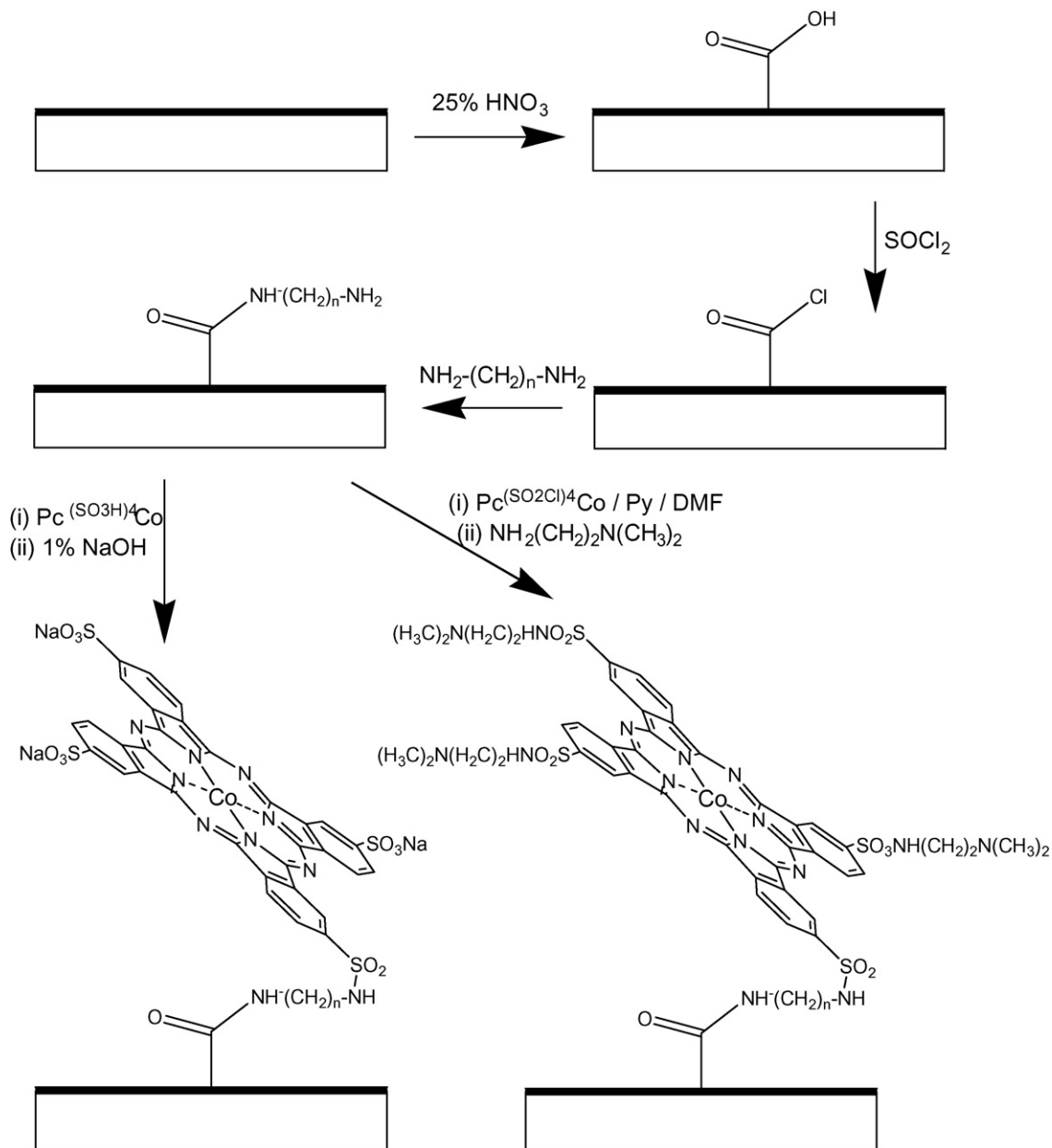[b] Percentage of unreacted carboxylic groups on the surface.

Fig. 2. Synthetic pathway for the preparation of SKN-*n*-N and SKN-*n*-H catalysts.

result, all of the SKN-*n*-N and SKN-*n*-H catalysts have both catalytically active cobalt phthalocyanine centers and basic aminogroups on the surface of catalysts and thus can be clearly considered as bifunctional heterogeneous systems. In present investigation, the concentration of immobilized sulfonated phthalocyanines was kept low in order to minimize possible formation of phthalocyanine dimers on the surface of catalysts, while an influence of the higher concentrations of the sulfonated phthalocyanines immobilized on the surface of SKN-*n*-H and SKN-*n*-N systems on their catalytic activity will be discussed in separate paper.

First, six SKN-*n*-H and SKN-*n*-N systems (*n* = 3, 5, and 7) were prepared and tested as catalysts in the 1-dodecane thiol autoxidation reaction. Based on the obtained data, two additional catalytic systems (SKN-4-H and SKN-4-N) have been

prepared and characterized. In spite of the expected high catalytic activity of SKN-2-H and SKN-2-N systems, these were not targeted because of the well-known technological difficulties in the preparation of extra dry 1,2-ethylenediamine.

3.2. Catalytic activity of heterogenic systems

The activity of new heterogeneous catalysts has been tested using the autoxidation reaction of dodecane-1-thiol. We prefer to use this highly hydrophobic thiol rather than more commonly used sodium sulfide of 2-mercaptoethanol because in the real life conditions, i.e. the Merox process, only the hydrophobic thiols should be oxidized by the catalyst [27] and the oxidation ability of the substituted cobalt phthalocyanines differs significantly for the oxidation of water-soluble thiols in aqueous media or
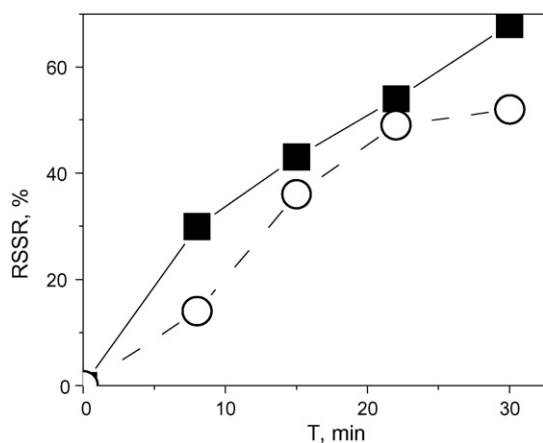
Fig. 3. Autoxidation of dodecane-1-thiol by SKN-5-N (squares) and SKN-5-H (circles) catalysts as a function of time.
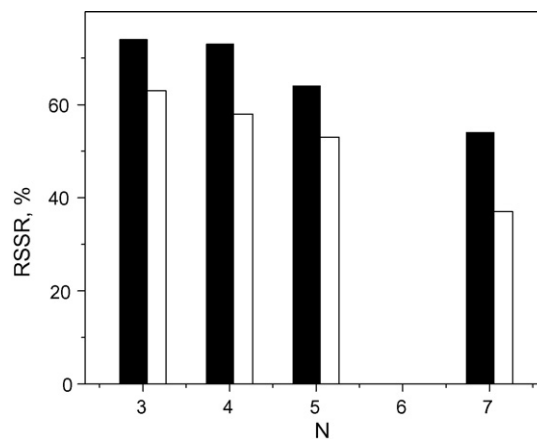

Fig. 4. Autoxidation of dodecane-1-thiol by SKN-n-N (solid bars) and SKN-n-H (open bars) catalysts in octane as a function of the linking group length ($t = 30$ min, $T = 50$ °C).

hydrophilic solvents as compared to the oxidation of hydrophobic thiols in non-polar organic solvents [28]. Furthermore, it has been mentioned that the rate of the thiol oxidation depends not only on the nature of the catalyst, but also on the length of the hydrophobic part of the thiol [5,8]. First, autoxidation of the dodecane-1-thiol using SKN-5-N and SKN-5-H catalysts has been investigated as a function of time (Fig. 3). It has been found that a more basic SKN-5-N catalyst exhibits a higher overall activity as well as reaction rate as compared to a less basic SKN-5-H analogue (Table 2). The data for other tested SKN-n-H and SKN-n-N catalysts are shown in Fig. 4. Clearly, for every given n, the SKN-n-N systems resulted in a better yield of the disulfide as well as reaction rates as compared to the respective SKN-n-H catalysts (Table 2). Taking into account that the concentration of the cobalt phthalocyanine complexes was found to be approximately the same for the respective SKN-n-H and SKN-N catalysts, the difference in the catalytic activity can be explained only on the basis of different concentration of aminogroups on the surface of catalysts. Indeed, every molecule of cobalt phthalocyanine in SKN-n-N systems introduces three additional basic centers (–SO$_2$NH(CH$_2$)$_2$N(CH$_3$)$_2$) to the catalyst's surface. It is generally accepted that the first step in the Merox process requires the deprotonation of the thiol by a Lewis base [5,29]:

$$RSH + :B = RS^- + HB^+$$
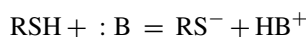
Following this assumption, an increase in the concentration of the basic groups located near the redox active cobalt center may increase the rate of dodecane-1-thiol ionization and thus increase the overall reaction rate.

The second interesting observation is that the yield of the desired disulfide dramatically decreases with increasing of n, which represents the length of anchoring diamine and the same tendency has been observed for the reaction rates (Table 2). Indeed, the highest overall yield of the target disulfide has been observed for the SKN-3-N and SKN-3-H catalysts (for the SKN-n-N and SKN-n-H catalysts, respectively). The relative catalytic activity (per substituted cobalt phthalocyanine molecule) of SKN-n-N and SKN-n-H heterogeneous systems shows the same trend: the smaller the length of the linking group, the higher the activity of the respective catalyst. The accepted reaction mechanism for the Merox process requires the formation of a highly unstable Co^I–•SR pair [5], which can be stabilized by a highly efficient electron buffer, i.e. carbon surface [22]. In this respect, shorter carbon–phthalocyanine distances should lead to a greater stabilization of the Co^I–•SR pair and thus result in a higher cat-

Table 2
Catalytic activity of heterogeneous systems in the autoxidation of dodecane-1-thiol in octane[a]

Catalyst	C_{Pc} ($\times 10^{-6}$ mol/g)[b]	RSSR (%)	k (s^{-1})	Moles of oxidized thiol ($\times 10^{-4}$)	C_{RSH}/C_{Pc}
SKN-3-N	4.2	74	2.2	3.98	945.1
SKN-4-N	4.2	73	2.2	3.93	933.7
SKN-5-N	3.9	64	1.8	3.44 (14.85[c])	893.3 (3856.1[c])
SKN-7-N	3.3	54	1.6	2.91	892.1
SKN-3-H	4.3	63	1.8	3.39	789.1
SKN-4-H	4.3	58	1.7	3.12	726.1
SKN-5-H	4.0	53	1.6	2.85 (10.81[c])	720.4 (2732.6[c])
SKN-7-H	3.4	37	1.1	1.99	587.9

[a] The raction conditions: 100 mg of catalyst, 10 ml of 5.38×10^{-2} M solution of dodecane-1-thiol, 50 °C, 30 min.
[b] Concentration of phthalocyanine centers per gram of carbon catalyst.
[c] Total amount for six experiments, see Section 2 for details.
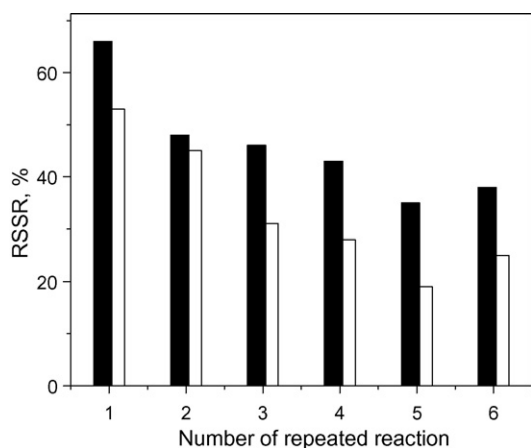
Fig. 5. Autoxidation of dodecane-1-thiol by SKN-5-N (solid bars) and SKN-5-H (open bars) catalysts in octane as a function of the number of catalytic cycles.

alytic activity of the respective heterogeneous systems. From the data presented above, it should be expected that the SKN-2-N and SKN-2-H catalysts will have even higher activity. However, unlike anhydrous $n = 3$–7 diamines, anhydrous ethylenediamine is relatively expensive for the industrial use and thus SKN-2-H and SKN-2-N systems have not been prepared.

The poisoning of the SKN-n-N and SKN-n-H systems has been tested using SKN-5-N and SKN-5-H samples (Fig. 5). In both cases, the catalytic activity gradually decreases as a function of numbers of catalytic cycles. One of the possible reasons, which can lead to the decrease of catalytic activity can be the protonation of the surface-located aminogroups by sulfinic acids, which are often reported as by-products in the Merox process [30]. In this case, treatment of the catalyst with a strong base should restore the activity. Indeed, treatment of the SKN-5-N and SKN-5-H systems with sodium hydroxide increases the activity of these catalysts for about ten percent (Fig. 6). This increase, however, is far smaller than expected for the complete regeneration of the protonated centers on the surface of a heterogeneous catalyst. This observation proves that

protonation does not play a major role in catalyst poisoning and probably reflects significantly more complex mechanism, which in part includes the degradation of phthalocyanine macrocycle. The leaching of sulfonated phthalocyanine may be another reason for observed degradation of catalysts. The characteristic phthalocyanine spectrum, however, has never been observed during catalytic cycles with SKN-n-H and SKN-n-H systems and thus, taking into account extremely low ($<1 \times 10^{-7}$ mol/l, determined by UV–vis spectroscopy) solubility of immobilized phthalocyanines in octane, the possibility of leaching should be negligibly small. In order to assure that the possible physical adsorption of sodium hydroxide during the catalyst preparation process is not responsible for the increase of the catalytic activity we conducted the catalyst treatment with the sodium hydroxide before the catalytic cycle on the fresh SKN-5-H and SKN-5-H catalysts and found that the catalytic activity was almost the same as in fresh SKN-5-N and SKN-5-H systems (Fig. 6).

4. Conclusions

Several bifunctional heterogeneous catalysts consisting of peripherally substituted cobalt phthalocyanine complexes covalently linked to the synthetic carbons modified by organic aminogroups have been prepared and tested in the catalytic reaction of the autoxidation of dodecane-1-thiol in organic solvents. It has been shown that the catalytic activity of heterogeneous SKN-n-N systems is higher as compared to the respective SKN-n-H line and probably reflects the difference in the surface aminogroup concentration. The absolute as well as relative catalytic activity of the heterogeneous catalysts decreases with the increase of the length of the linker for both series tested. The catalysts remain active for several catalytic cycles, in spite of the observable decrease in their activity. A partial regeneration of the catalytic activity can be achieved using the treatment of respective catalysts with diluted solutions of sodium hydroxide, while no improvement in the catalytic activity has been observed when the fresh catalysts were treated with sodium hydroxide prior to the catalytic reactions.
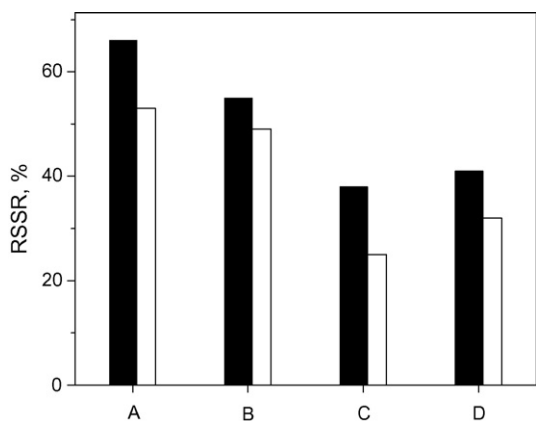
Fig. 6. Autoxidation of dodecane-1-thiol by SKN-5-N (solid bars) and SKN-5-H (open bars) catalysts in octane. (A) By fresh catalysts; (B) by fresh catalysts treated with 5% NaOH; (C) by catalysts after six catalytic cycles; (D) by catalysts after six catalytic cycles regenerated by treatment with 5% NaOH.

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