Oxidation of 2-mercaptoethanol catalyzed by cobalt(II) phthalocyaninetetrasulfonate supported on poly-*N*-alkyl-4-vinyl pyridinium/montmorillonite intercalates

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Abstract

Cobalt(II) phthalocyaninetetrasulfonate supported on poly-*N*-alkyl-4-vinyl pyridinium/montmorillonite intercalates were prepared and used as catalysts for the oxidation of 2-mercaptoethanol in aqueous medium. Cobalt(II) phthalocyaninetetrasulfonate supported on polymer–clay intercalates (**5**–**8**) showed good catalytic activity in the autoxidation of 2-mercaptoethanol to disulfide. The rate of reaction was found to fit a Michaelis–Menten kinetic model for saturation of catalyst sites with increasing thiol concentration. Recycling of the catalyst CoPcTS/clay–polymer system **6** showed good stability up to three consecutive runs and then the reactivity declined by the fourth run.
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1. Introduction

The scope of heterogeneous catalytic organic transformations is rapidly growing due to their well-documented advantages over homogeneous catalytic systems [1]. Clays have emerged as ideal acidic heterogeneous catalysts as they are available in nature and are thus inexpensive. These clays have Brønsted as well as Lewis acidic sites and thus increase their utility in both types of catalytic applications [2,3]. Also, clays exhibit specific features such as high versatility, wide range of preparation variables, high stability, use in catalytic amounts, ease of set-up and work-up, mild experimental conditions, gain in yield and/or selectivity, ease of handling and regeneration, non-corrosiveness, low cost, etc., which may be very useful tools in the move towards establishing environmentally friendly technologies [2–6].

Selective organic transformation in the presence of various solid catalysts including metal cation-exchanged clays is of current interest in making the synthetic processes comfortable and benign to the earth [7–9].

The oxidation of sulfur-containing compounds such as mercaptans, alkali sulfides and thiosulfates is important for eliminating offensive odor (MEROX process) of petroleum products and necessary for the treatment of industrial and domestic waste waters [10]. Metal phthalocyanines bound or anchored on different supports such as polyelectrolytes, anion exchange resins, layered clays, silica and cationic latexes are excellent catalyst for the oxidation of thiols with dioxygen [11].

The aim of this work is to investigate the potential use of polymer–clay intercalates exemplified by polyvinylpyridinium–montmorillonite intercalates as support for cobalt(II) phthalocyaninetetrasodiumsulfonate in the catalytic oxidation of 2-mercaptoethanol.

2. Experimental

2.1. Materials and reagents

Poly(4-vinylpyridine) M_w: 10,000 was obtained from Polysciences and was used as received. Montmorrilonite clay

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(mineral colloid-BP) was a gift from ECC America Inc. with cation exchange capacity (CEC) of 114.8 meq/100 g. 2-Mercaptoethanol (98%) Aldrich was distilled and stored in the dark.

Buffer solutions were prepared as follows. The pH 7.0 was adjusted using a mixture of 0.025 M Na_2HPO_4 and 0.10 M HCl while pH 8.0 and 9.0 were adjusted by using sodium borate and HCl mixture.

2.2. Measurements

Microanalysis was performed by Microanalysis Center at Cairo University and Microanalysis Unit at Tanta University, Egypt. IR spectra were recorded on Perkin-Elmer 1420 spectophotometer using KBr disc technique. X-ray diffraction data were obtained using Phillips 1729 diffractometer with Cu K ($\lambda = 1.54180$ nm) as the X-ray source. The polymer–clay intercalates were scanned at $2\theta = 2°-18°$.

2.3. Preparation of polymeric pyridinium salts 1–4

Poly(4-vinylpyridinium) salts (**1–4**) have been prepared by treatment of poly(4-vinylpyridine) with different alkyl halides; methyl iodide, *n*-butyl bromide, *n*-octyl bromide and *n*-hexadecyl bromide, respectively, according to previously published procedure [12].

2.4. Preparation of polymeric pyridinium salts–clay intercalates 5–8

The preparation of poly(*N*-methyl-4-vinyl pyridinium iodide)-clay intercalate **5** is typical: To polymeric salt 1 (1.97 g, 8.0 mmol) dissolved in 50 ml of water 5.0 g of sodium montmorillonite (MMT-ONa$^+$) was added as aqueous suspension. The reaction mixture was stirred at room temperature. The solid product was isolated by centrifugation and washed thoroughly with distilled water till no halide detected in the filtrate to give 5.42 g (84%) of polymer–clay intercalate **5**. Elemental microanalysis indicated 2.70% N.

Polymer–clay intercalate **6**: yield 5.61 g (86%). Elemental microanalysis: 1.70% N.
Polymer–clay intercalate **7**: yield 5.70 g (85%). Elemental microanalysis: 5.2% N.
Polymer–clay intercalate **8**: yield 6.80 g (92%). Elemental microanalysis: 5.0% N.

The X-ray diffraction pattern of poly(*N*-butyl-4-vinylpyridinium/MMT) **6** and poly(*N*-hexadecyl-4-vinylpyridinium/MMT) **8** (Fig. 1) showed basal plane expansion to 13.708 and 14.243 Å, respectively, from 9.6 of dehydrated sodium montmorillonite. The I.R. spectrum of the polymeric pyridinium salt **2** and polymer–clay intercalate **6** showed the appearance of a bands at 1631–1460 cm^{-1} corresponding to (C–C) and (C–N) ring stretching of pyridines [13].
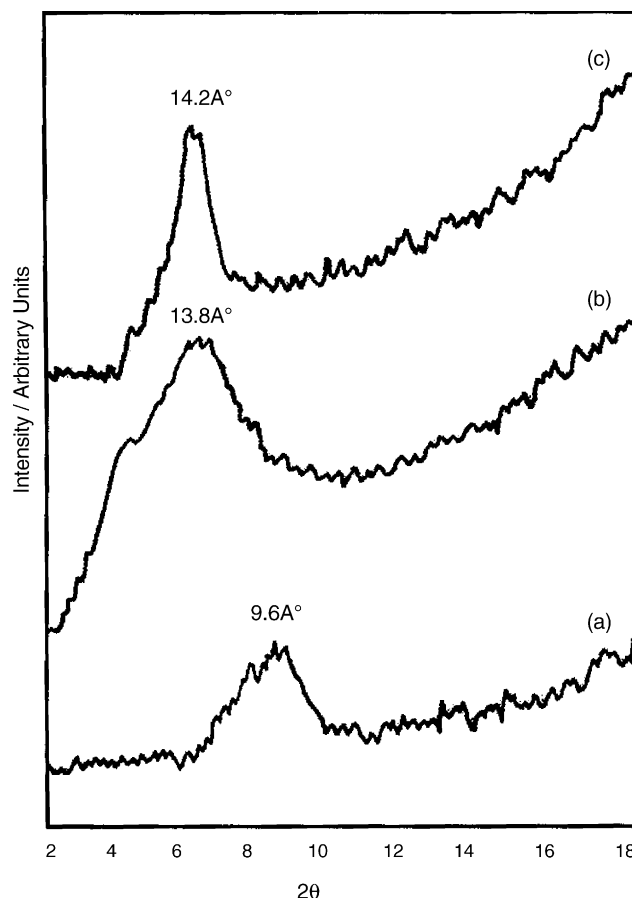

Fig. 1. X-ray diffraction patterns of: (a) sodium montmorillonite (MMT-ONa); (b) poly(*N*-butyl-4-vinylpyridinium)/MMT **6**; (c) poly(*N*-hexadecyl-4-vinylpyridinium)/MMT **8**.

2.5. Oxidation of 2-mercaptoethanol

The oxidations of 2-mercaptoethanol (2-ME) were performed at 35.0 °C and dioxygen pressure of 750 ± 4 mmHg as described previously [11]. In experiments where lower dioxygen pressure used; the low pressure was obtained by using nitrogen/oxygen mixtures at 750 mmHg total pressure. Rate of reactions was monitored using gas burette. The reaction product was extracted from reaction mixture using chloroform and was identified by comparison with authentic sample. About 95% yield of the disulfide was obtained in the oxidation reaction carried out using clay-intercalate **6**.

3. Results and discussion

Polymer–clay intercalates (**5–8**): were prepared by reacting a solution of the polymeric pyridinium salt (**1–4**) with aqueous suspension of the sodium montmorillonite (MMT-ONa) clay (Scheme 1).

Proof of binding of the polymeric pyridinium salts to clay came from X-ray diffraction, IR spectra and elemental microanalysis.
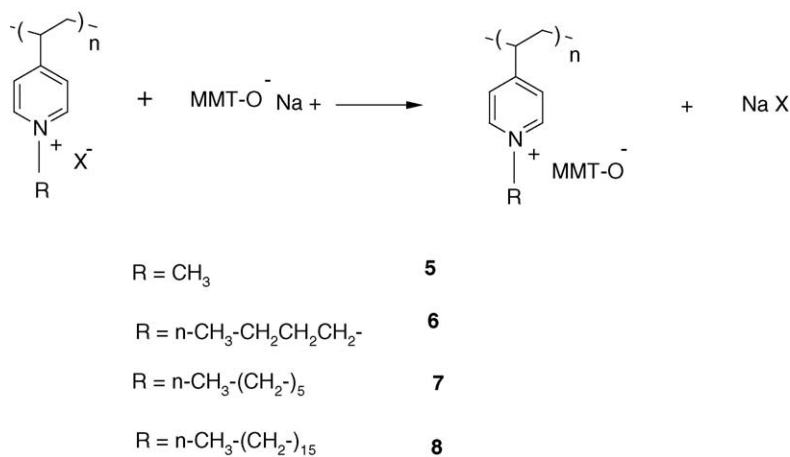
Scheme 1.

The X-ray diffraction patterns of poly(*N*-butyl-4-vinylpyridinium)/MMT **6** (Fig. 1b) and poly(*N*-hexadecyl-4-vinylpyridinium)/MMT **8** (Fig. 1c) showed basal plane expansion to 13.798 and 14.243 Å, respectively, from 9.6 Å of dehydrated sodium montmorillonite. The basal spacing d_{001} of 13.798 and 14.243 Å corresponds to interlamellar spacing of 4.498 and 4.943 Å, respectively. These results indicate that the polymeric pyridinium salts have accessed the interlamellar spacing of the mineral giving polymeric pyridinium salts–clay intercalates.

3.1. Oxidation of 2-mercaptoethanol

The catalytic activity of cobalt(II) phthalocyanine-tetrasodiumsulfonate (CoPcTSNa$_4$) in presence of montmorillonite-polymeric pyridinium salts intercalates **5**–**8** as co-catalysts was investigated in the autoxidation of 2-mercpto-ethanol to disulfide. Autoxidation reactions were performed with vigorous magnetic stirring of the reaction mixture under 0.97 atm pressure of dioxygen in a flask connected to a gas burette. Gas burette measurements of dioxygen consumption was used to follow the kinetics of autoxidation reactions, 4 mol of 2-mercaptoethanol were consumed per 1 mol of dioxygen, which corresponds with the stoichiometry of the following equation:

$$4HO-CH_2-CH_2-SH + O_2$$
$$\rightarrow 2(HO-CH_2-CH_2-S)_2 + 2H_2O$$
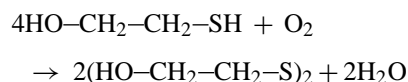
Measurements of dioxygen consumption of the autoxidation reactions showed that after short induction period, the volume of dioxygen consumed was linear with time. Therefore, the rate law has a zero-order dependence on substrate concentration.

Data for catalytic activities of soluble (CoPcTSNa$_4$) and CoPcTSNa$_4$/polymeric pyridinium salts-intercalates (**5**–**8**) in the autoxidation of 2-mercaptoethanol are summarized in (Table 1).

All of polymer/clay supported catalysts were more active than soluble CoPcTSNa$_4$. The most active catalyst was CoPcTSNa$_4$ supported on poly(*N*-butyl-4-vinyl-pyridinium)/MMT **6** which was about three times as active as soluble CoPcTSNa$_4$.

The higher activity of CoPcTSNa$_4$ supported on polymer–clay intercalates (**5**–**8**) may be attributed to a higher concentration of 2-mercaptoethanol in the polymer–clay intercalates, the phase that contains the active sites [14].

Further investigation of various reaction conditions in the autoxidation of 2-mercaptoethanol was carried out using CoPcTSNa$_4$ as catalyst and poly(*N*-butyl-4-vinylpyridinium)/MMT **6** as co-catalyst.

3.2. Effect of pH on the autoxidation of 2-mercaptoethanol

The autoxidation of 2-mercaptoethanol was studied in the pH range 7.0–9.0 using sodium borate and sodium phosphate buffers (Table 2). It was found that the zero-order rate constant k_{obs} was increased with increasing the pH value of reaction medium.

Table 1

Autoxidation of 2-mercaptoethanol catalyzed by cobalt(II) phalocyninete-trasodiumsulfonate and polymer–clay intercalates[a]

Catalyst	$10^4 \, k_{obs}$ (mol/L/min)[b]
CoPcTSNa$_4$	0.680
CoPcTS + 5	0.840
CoPcTS + 6	2.140
CoPcTS + 7	0.860
CoPcTS + 8	0.850

[a] All reactions were carried out at 35 °C and dioxygen pressure of 740 mmHg with magnetic stirring of 14.2 mmol of 2-mercaptoethanol and 1×10^{-5} M of CoPcTSNa$_4$ and 0.09 mmol of support. The total volume of reaction mixture was maintained at 200 ml. The pH was adjusted to 9.0 using borate buffer.

[b] Zero-order rate constant calculated from the plot of thiol consumption vs. time.

Table 2
Effect of pH on the rate of autoxidation of 2-mercaptoethanol[a]

pH[b]	10^4 k_{obs} (mol/L/min)[c]
7.0	0.900
8.0	1.160
9.0	1.660

[a] Reactions were carried out using 0.5×10^{-5} M CoPcTSNa$_4$ and 0.09 mmol of poly(N-butyl-4-vinylpyridinium)/MMT 6. Other reaction conditions are reported in Table 1.
[b] The pH 7.0 was adjusted using a mixture of 0.025 M Na$_2$HPO$_4$ and 0.10 M HCl while pH 8.0 and 9.0 were adjusted using sodium borate and HCl mixture.
[c] Zero-order rate constant calculated from the plot of thiol consumption vs. time.

The increase of initial zero-order rate constant k_{obs} of autoxidation of 2-ME catalyzed by CoPcTSNa$_4$ in presence of polymer–clay intercalate 6 with increasing the pH from 7.0 to 9.0 (Table 2) indicates that the thiolate anions RS$^-$ is the active species [10,14].

3.3. Effect of [CoPcTSNa$_4$] on the autoxidation of 2-mercaptoethanol

The dependence of the initial rate constant k_{obs} on the concentration of CoPcTSNa$_4$ was investigated in the concentration range (0.25×10^{-5} to 1.5×10^{-5} M), while the concentration of clay–polymer intercalate 6 was kept constant at 0.09 mmol. The plot in (Fig. 2) shows the linear increase of rate constants k_{obs} with increasing the concentration of CoPcTSNa$_4$.

Without catalyst CoPcTSNa$_4$, in presence of the intercalate 6 only the activity was very low (Fig. 2).
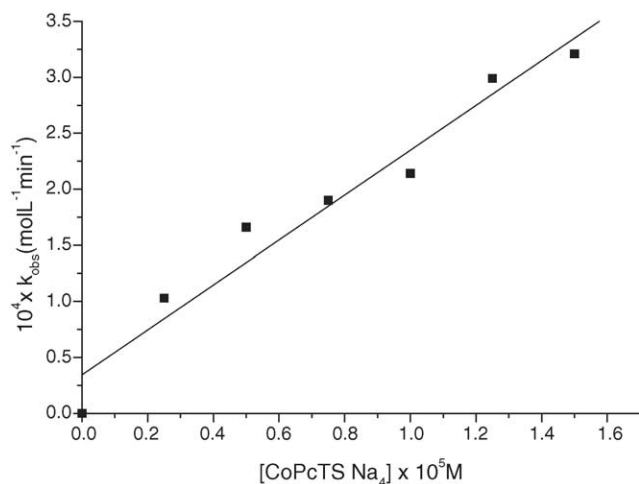

Fig. 2. Dependence of rate constant on CoPcTSNa$_4$ concentration. For reaction conditions, see footnote of (Table 1). Reactions were carried out using 0.09 mmol of poly(N-butyl-4-vinylpyridinium)/MMT 6.
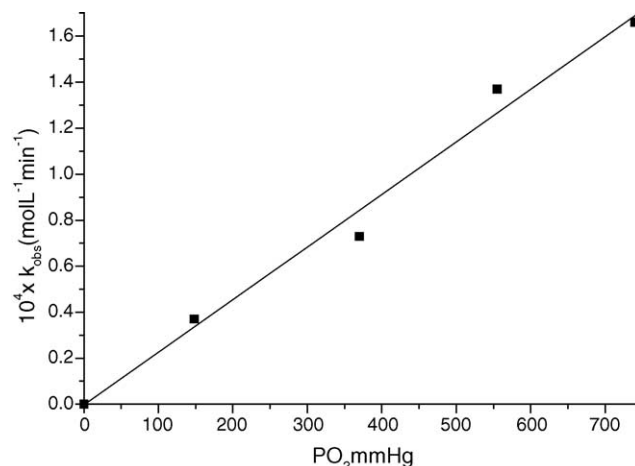

Fig. 3. Dependence of the rate constant k_{obs} in autoxidation of 2-ME on partial pressure of dioxygen. For reaction conditions, see footnote of (Table 1), unless noted otherwise. All reactions were carried out using (0.5×10^{-5} M) of CoPcTSNa$_4$ and 0.09 mmol of poly(N-butyl-4-vinyl pyridinium)/MMT 6.

3.4. Effect of partial pressure of dioxgyen on the autoxidation of 2-mercaptoethanol

The effect of the partial pressure of dioxygen was investigated by using oxygen/nitrogen mixture to obtain reduced partial pressure of 1 atm total pressure on the reaction mixture.

The plot in (Fig. 3) shows the linear increase of rate constants k_{obs} with increasing the partial pressure of dioxygen.

The linear dependence of initial rate constant k_{obs} on the concentration of cobalt(II) phtalocyaninetetrasulfonate and on the pressure of dioxygen indicate that the rate of autoxidation of 2-ME is not limited by mass transfer or intraparticle diffusion of dioxygen or RS$^-$ to the active site in the polymer–clay particles. Moreover, the clay–polymer intercalate 6 forms a colloidal dispersion in water, due to their small particle size <1 μm in diameter. This assists the rapid transport of reactants to the internal catalytic sites, and consequently reduces the effect of intraparticle diffusional limitations.

3.5. Effect of concentration of polymer–clay intercalate on the rate of autoxidation of 2-mercaptoethanol

The concentration of poly(N-butyl-4-vinylpyridinium) /MMT 6 was varied systematically while the concentration of CoPcTSNa$_4$ was kept constant. Data summarized in (Table 3) show the maximum activity at 0.09 mmol of the polymer–clay intercalate 6.

The maximum in the rate constant of autoxidation of 2-ME with varying the concentration of catalyst support 6 at constant CoPcTSNa$_4$ concentration shown in (Table 3) has been also observed before for the autoxidation of 2-ME with CoPcTSNa$_4$ in ionenes [15] and with cationic micellar catalysts [17]. The increase in rate with up to 0.09 mmol of

Table 3
Effect of poly(*N*-butyl-4-vinylpyridinium)/MMT **6** concentration on the rate of autoxidation of 2-mercaptoethanol[a]

Poly(*N*-butyl-4-vinyl-pyridinium)/MMT **6**	$10^4\ k_{obs}$ (mol/L/min)[b]
0.060	0.950
0.090	1.660
0.012	1.450
0.240	1.040
0.480	0.950

[a] All reactions were carried out under conditions reported in (Table 1) unless noted otherwise reactions were carried out using (0.5×10^{-5} M) of CoPcTSNa$_4$.
[b] Zero-order rate constants calculated from the plot of thiol consumed vs. time.

catalyst support **6** could be attributed to increasing of the concentration of 2-ME in the catalyst phase. The decrease in rate constant with 0.48 mmol of catalyst support could be attributed to a decreased concentration of CoPcTS in polymer–clay phase.

3.6. Effect of concentration of 2-mercaptoethanol on the rate of autoxidation

The dependence of rate constant k_{obs} of autoxidation reaction on the concentration of 2-mercaptoethanol was investigated in the concentration range 0.028–0.17 mol/L (Fig. 4). The initial rate constant k_{obs} increased with increasing concentration of 2-ME and then leveled off at 0.070 mol/L.

The initial zero-order rate constants of autoxidation of 2-ME depend on initial 2-mercaptoethanol concentration as shown in (Fig. 4). A double reciprocal lineweaver–Burk plot (Fig. 5), for the data of (Fig. 4) shows that the data fit a Michaelis–Menten kinetic model for saturation of catalyst sites with increasing thiol concentration. These results suggest that Michaelis–Menten mechanism can be described for the autoxidation of 2-mercaptoethanol (Scheme 2). Similar
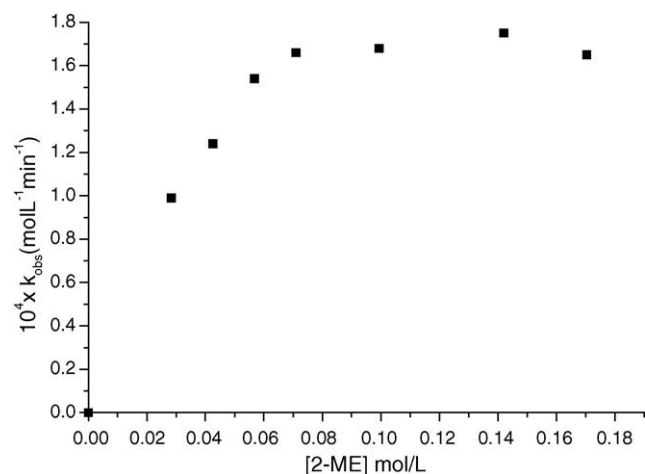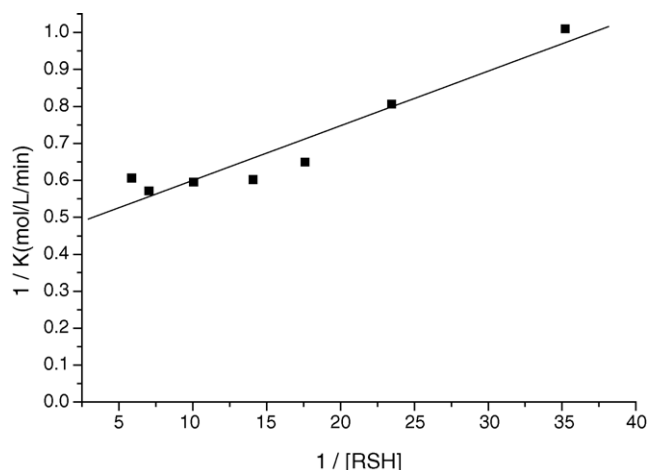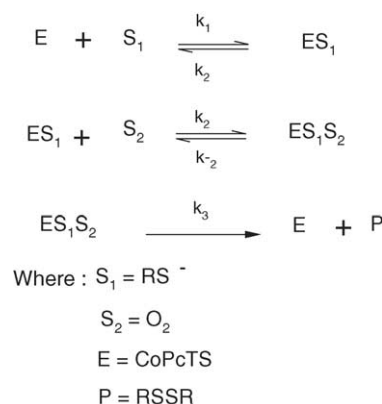
Fig. 5. Lineweaver–Burk plot of the data in Fig. 4.

mechanism has been reported for the oxidation of thiols catalyzed by cobalt(II) phthalocyaninetetrasulfonate [16].

3.7. Catalyst re-use

Reuse of the catalyst CoPcTSNa$_4$ in presence of poly(*N*-butyl-4-vinylpyridinium)/clay intercalate **6** was tested as follows, autoxidation of 2-mercaptoethanol was carried out under standard reaction conditions of (Table 1) using 1.250×10^{-5} M of CoPcTSNa$_4$. The reaction was followed by dioxygen uptake. After the completion of the first run, the initial amount of 2-mercaptoethanol was again fed into reaction mixture without removal of the reaction products. Data illustrated in (Fig. 6) showed that after five successive runs the catalyst activity was 0.33 times as active as the fresh catalyst.

Recycling of the catalyst CoPcTSNa$_4$/clay–polymer system **6** showed reduced activities after four successive runs. Since this occurred without extraction of the reaction products between kinetic runs, deactivation could be attributed to accumulation of reaction products in the clay/polymer intercalate near the active site. Also possibly by-products convert the CoPcTSNa$_4$ to some catalytically inactive species [14].
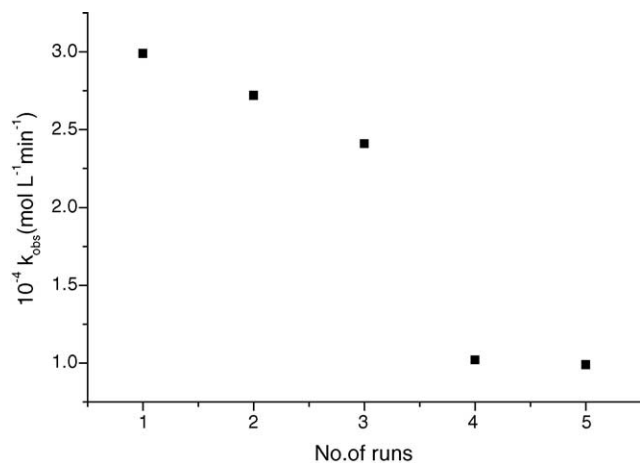
Fig. 4. Dependence of rate constant k_{obs} on 2-ME concentrations. For reaction conditions, see footnote of Fig. 3.

$$E\ +\ S_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES_1$$

$$ES_1\ +\ S_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ES_1S_2$$

$$ES_1S_2 \overset{k_3}{\longrightarrow} E\ +\ P$$

Where : S_1 = RS$^-$

S_2 = O$_2$

E = CoPcTS

P = RSSR

Scheme 2.

Fig. 6. Catalyst re-use in the autoxidation of 2-ME. Reactions were carried out using 1.250×10^{-5} M CoPcTSNa$_4$.

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