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Bivalent copper oligopyrocatecholate as a novel heterogeneous catalyst for the oxidative degradation of mercaptan in caustic solution: Synthesis, characterization, and kinetic study

R.M. Akhmadullin^a, A.T. Gubaidullin^b, Kh. E. Kharlampidi^c, S.R. Kurbankulov^c, T. F. Nigmatullin^c, M.U. Dao^{d,e,**}, R.F. Khamidullin^c, A.G. Akhmadullina^a, Y. Vasseghian^f, H. Y. Hoang^{g,*}

^a R&D "AkhmadullinS" LLC, 34 Syberian Tract, Kazan, 420139, Russia

^b A.E. Arbuzov Institute of Organic and Physical Chemistry, 8 Akad. Arbuzova, Kazan, 420088, Russia

^c Kazan National Research Technological University, 68 Karl Marx, Kazan, 420015, Russia

^d Center for Advanced Chemistry, Institute of Research and Development, Duy Tan University, Da Nang, 550000, Viet Nam

^e The Faculty of Natural Sciences, Duy Tan University, Danang, 550000, Viet Nam

^f Department of Chemical Engineering, Quchan University of Technology, Quchan, Iran

^g Ho Chi Minh City University of Natural Resource and Environment, Ho Chi Minh, 72110, Viet Nam

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ABSTRACT

A novel catalyst based on bivalent copper oligopyrocatecholate was first successfully synthesized and dispersed in a polymer matrix for oxidative degradation of mercaptan in aqueous caustic solution. X-ray diffraction analysis has demonstrated that the synthesized catalyst was a crystalline phase with a minimum amorphous component. Mechanism analysis and kinetic experiments were conducted to investigate the kinetic mechanism of the reaction of isopropyl mercaptan oxidation catalyzed by copper oligopyrocatecholate dispersed in a polymer matrix. The influences of temperature, initial concentrations of reactants, and catalytic surface area on the reaction rate were studied to obtain the rate expression of intrinsic kinetics. The research results showed that the subsequent electron-transfer step was the rate-limiting step of the reaction. Additionally, the mercaptan oxidation rate in caustic solution was inversely proportional to the first power of the alkali concentration. The apparent activation energy was approximately 27.71 ± 1.12 kJ/mol. Importantly, this rate law for mercaptan oxidation can be used to design industrial reactors for the light oil sweetening process.

1. Introduction

The pollution of sulfur-containing volatile organic compounds is a significant environmental problem. In addition to its carcinogenic potential, the toxic compound can also lead to the formation of secondary pollutants, such as tropospheric ozone, peroxyacetyl nitrate, and secondary organic aerosols (He et al., 2019). Today, one of the most problematic sulfur-containing volatile compounds is mercaptan (R-SH), widely distributed in petroleum products and industry off-gases. Although mercaptan presented in gases for energy applications is deliberately added as a safety precaution due to their low odor thresholds, even a tiny amount of mercaptan in the atmosphere can adversely

affect humans and corrode metal equipment (Cui et al., 2019). Therefore, if mercaptan has a high concentration in natural gas, it must be removed to reduce the value to an acceptable limit. The gas sweetening process is regarded as the most effective method for the complete removal of mercaptan as it is both economically and environmentally feasible (Ling et al., 2021). In this process, mercaptan could be absorbed into the liquid caustic soda and then rapidly oxidized to innocuous disulfides by air oxygen in the presence of a catalyst.

Among numerous catalyst types developed for aerobic oxidation of mercaptan, transition metals and their compounds are the most commonly known. Most inorganic compounds of a transition metal such as metal alloys (Gao et al., 2009), mixed metal oxides (Akhmadullin

* Corresponding author. Ho Chi Minh City University of Natural Resources and Environment, Ho Chi Minh, 72110, Viet Nam.

** Corresponding author. Center for Advanced Chemistry, Institute of Research and Development, Duy Tan University, Da Nang, 550000, Viet Nam.

E-mail addresses: daomyuyen@duytan.edu.vn (M.U. Dao), hhy@hcmunre.edu.vn (H.Y. Hoang).

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et al., 2013; Chen et al., 2016; Mei et al., 2007; Zhu and Yu, 2021), natural metal ores (Li et al., 2012; Menini et al., 2011) and inorganic transition metal complexes (Wallace et al., 1964) are considered potential catalysts in mercaptan oxidation.

Organometallic compounds have long been attracted the attention of the catalysis community due to their excellent catalytic activity and a wider range of applications in interdisciplinary subject areas (Kumar et al., 2019). Transition metal phthalocyanines and their derivatives are among the most effective organometallic compounds used to catalyze mercaptan oxidation in the petroleum refining industry for a long time (Motahari et al., 2020; Scott et al., 2019). To this day, research and development of a new type of organometallic compound have still been actively underway to improve its catalytic activity in mercaptan removal (Gantman et al., 2016; He et al., 2019; Lutkus et al., 2017; Shahmoradi et al., 2020). Pyrocatechol, containing hydroxyl groups fundamentally capable of coordinating to transition metal in three different oxidation states, occupies a special position not only in the formation of organometallic chemistry but also in catalysis (Broere et al., 2015). Transition metal pyrocatecholates are often characterized by attractive electronic or magnetic properties, which in turn lead to their diverse potential applications (Ershova et al., 2020). The utility of redox-active catechol and its derivatives has expanded rapidly during the last few years to include applications in organometallic catalyst synthesis (Broere et al., 2015).

In addition, oligomerizing a compound to form a reactive polymeric reagent that possesses both the beneficial physical properties of a high polymer and the chemical properties of constitutive monomer is becoming an increasingly important aspect of organometallic chemistry. The advantages of oligomers over conventional low-molecular-weight reagents have been critically discussed many times before. Furthermore, oligomers often overcome many of the inconvenient properties of monomeric species, such as toxicity, lability, volatility, and odor (Lawrance, 2010). As a result, oligomers have been rapidly developed from a novel research field into a key one in recent years, making valuable contributions to catalysis and other scientific fields.

Therefore, a project has been proposed by us to research and develop the transition metal oligopyrocatecholate based novel catalyst for the aerobic oxidation of mercaptan in the aqueous caustic solution. In this paper, the synthesis of bivalent transition metal oligopyrocatecholate was first reported, and its catalytic activity was evaluated in the oxidative degradation of mercaptan. Additionally, the kinetics and mechanism of catalysis were further studied.

2. Experimental section

2.1. Chemicals and materials

In our experiments, all reagents were purchased from commercial sources and used as received unless otherwise indicated. They are as follows: NaOH (Russia, GOST 4328–77), CuSO₄·xH₂O (Russia, GOST, 19347–99), Na₂SO₄·10H₂O (Russia, GOST 21458–75), pyrocatechol C₆H₆O₂ (Russia, GOST 2472–13), 3,3',5,5'-tetra-tert-butyl-4,4'-diphenylquinone C₂₈H₄₀O₂ (Russia, TU 12.1.007–76), isopropyl mercaptan C₃H₈S (Russia, CAS 75-33-2), distilled water H₂O (Russia, GOST 6709–72), high-density polyethylene (Russia, GOST 16337–77), technical gaseous oxygen in cylinders (Russia, GOST 5583–78), and technical gaseous argon in cylinders (Russia, GOST 10157–79).

2.2. Catalyst synthesis

Bivalent copper oligopyrocatecholate (oligoCat-Cu) was prepared to evaluate the catalytic activity of bivalent transition metal in the aerobic oxidation of mercaptan. Pyrocatechol (Cat), playing the role of initial raw material, is first oxidatively polymerized into oligocatechol (oligoCat) which is following chemically modified with copper (II) sulfate solution to form oligoCat-Cu. The general scheme for oligoCat-Cu

synthesis is outlined in Fig. 1. According to that, catechol is oxidatively polymerized by 3,3',5,5'-tetra-tert-butyl-4,4'-diphenylquinone in the presence of sodium hydroxide-based catalyst at the high temperature (Nigmatullin et al., 2018). The synthesis was implemented in a cylindrical stainless steel reactor equipped with a pressure gauge and temperature control probe. The reaction mixture containing 5 g of 3,3',5,5'-tetra-tert-butyl-4,4'-diphenylquinone, 1.0 g of pyrocatechol, 1 mL of 10 wt% sodium hydroxide solution, and 50 mL of toluene was loaded into the reactor. The reaction solution was heated to 160 °C by a thermally controlled magnetic stirrer. Once the required temperature was reached, stirring was turned on, and the reaction mixture was maintained at a constant rotational speed of 1000 rpm for 30 min. Using the photocolometry method at $\lambda = 540$ nm, the catechol conversion was identified indirectly by the residual concentration of 3,3',5,5'-tetra-tert-butyl-4,4'-diphenylquinone. In addition, the concentration of 4,4'-bis(2,6-di-tert-butyl-phenol) formed during the synthesis was further determined by gas-liquid chromatography (GLC) and was 10,3 wt%, corresponding to 100% catechol conversion. After completing the synthesis time, the reactor was cooled to 85 °C. The precipitate of the resulting oligomer was separated from the aqueous phase by filtration, washed up with distilled water, and dried in vacuo at 70 °C until mass stabilization. The obtained oligoCat yield 86%. IR spectrum, ν , cm⁻¹: 3600 (OH), 1600, 1512 (C=Carom), 1350, 1250, 1180 (C–OH). Found, %: C 66.2; O 30.02; H 3.87. Calculated, %: C 66.01; O 29.25; H 4.74. The molecular weight of oligoCat identified by MALDI TOF mass spectrometry varies from 577 to 1421 (see Supplemental Fig. S1), corresponding to the number of units from 5 to 15.

The binding of copper ion to units of oligoCat was conducted to obtain oligoCat-Cu. The procedure includes two main stages: synthesis of sodium oligopyrocatecholate (oligoCat-Na₂) and cation exchange of oligoCat-Na₂ with CuSO₄ in aqueous solutions. The oligoCat-Na₂ synthesis was carried out in a 200 mL glass conical flask, into which an alkaline aqueous solution was prepared by dissolving 2.4 g (0,06 mol) of NaOH in 75 mL of distilled water and 3.24 g (0.03 mol) of oligoCat were added. The reaction mixture was magnetically stirred until oligopyrocatechol was completely dissolved. The cation exchange of sodium oligopyrocatecholate with transition metal salts was initiated when a saline solution containing 0.03 mol of CuSO₄ was loaded into the conical flask. The obtained mixture reaction was further stirred for 30 min. A black curdy precipitate, supposedly oligoCat-Cu, was formed during the reaction process and then filtered and dried under vacuum until mass stabilization (yield of 4.65 g).

2.3. Catalytic oxidation of mercaptan

Isopropyl mercaptan (C₃H₈S) was used as a representative of mercaptan to evaluate the catalytic activity of oligoCat-Cu in this study. Unless otherwise noted, the catalytic aerobic oxidation of mercaptan was performed under atmospheric conditions inside 150 mL of a three-neck-round-bottom flask with a magnetic stirring bar. Glass reactor was used to avoid any contact of the reaction solution with metals, which would accelerate the mercaptan oxidation. In a typical run, 50 mL of the aqueous caustic solution containing 10 wt% NaOH and a defined concentration of C₃H₈S was loaded into the reactor in the presence of a certain amount of the catalyst component. Preliminary experiments were conducted to verify the conversion of mercaptan to mercaptide ion (C₃H₇S⁻) in this solution. As a result, the mercaptan used under experimental conditions was in the form of sodium mercaptide (C₃H₇SNa). The reaction mixture was magnetically stirred and heated under a dry argon atmosphere until a given temperature was reached. The oxygen from the cylinder was then injected into the reaction mixture at a constant velocity. The outlet gas was first cooled by a condenser to prevent the steam in the reactor from being too hot to flow out and then enters the absorption system for harmless treatment. To study the kinetic mechanism of catalytic oxidation of C₃H₈S in the aqueous caustic solution, oxygen diluted in argon was continuously injected into the



Fig. 1. General scheme for the synthesis of copper oligopyrocatecholate.

reaction solution at 50–350 h⁻¹, the reaction solution was stirred at the speed of 500–1500 rpm, and its temperature was maintained in the range of 30–70 °C for the indicated time. The reaction was studied by the concentration variation of sodium mercaptide, determined by potentiometric titration by UOP method 209–00.

2.4. Catalyst characterization and analytical methods

Powder X-ray diffraction patterns (P-XRD) of catalyst were recorded on a Bruker D8 Advance X-ray diffractometer equipped with a Vario attachment and a Vantec linear coordinate detector. The Cu K α radiation ($\lambda = 1.54063 \text{ \AA}$) was monochromatized by a bent Johansson monochromator. X-ray tube operating mode of 40 kV and 40 mA was used. The diffraction patterns were collected at room temperature in the Bragg-Brentano geometry using a flat holder and over an angular range of 20° to 100° with a step size of 0.0081° per step and a dwell time of 0.1–4 s per increment. For each of the samples, several diffraction patterns were obtained in different experimental modes, with different data acquisition times as well as both for stationary samples and rotating in their plane at a speed of 15 rpm (to eliminate the effects of the preferred orientation of the sample particles). This made it possible to confirm the reproducibility experiments and obtain statistically reliable data. Powdered samples, pre-ground and sifted through a sieve (60 μm), were filled into a 2 mm deep cavity of a standard PMMA cuvette and aligned in it. In addition, their tablet forms (pre-compressed powders) were investigated for several samples, which were installed on a standard sample holder without preliminary preparation. The obtained data was collected and baselined using the Bruker DIFFRAC. EVA software suite v.110.0.3. The Powder Diffractionometry File (PDF-2) was used to identify the known crystalline phases. The full-profile analysis of powder diffraction patterns, their indexing, and the Rietveld refinement parameters were performed using the TOPAS and TOPAS I programs.

The molecular weight distribution of oligopyrocatechol was determined using a Bruker Daltonik MALDI TOF high-resolution mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix.

The particle morphology of the catalyst was observed on a Scanning Electron Microscope (SEM, ZEISS EVO 50 XVP with LaB6 source), working at an accelerated voltage of 20 kV and equipped with detectors for secondary electron as well as backscattered electron collection. Fourier-transform infrared (FT-IR) spectra were recorded as KBr pellets or as neat liquids using a PerkinElmer Spectrum Two FTIR spectrophotometer. The elemental analysis was performed using a Carl Zeiss AURIGA Cross Beam workstation equipped with an Oxford Instruments INCA-MAX energy-dispersive spectrometer (resolution 127 eV). The reaction mixtures were analyzed by GLC on a Khromatek Kristall-5000 gas chromatograph. Meanwhile, the conversion of diphenolquinone was established using spectrophotometry (Eros PE5300V, regime A, wavelength $\lambda = 540 \text{ nm}$, path length $L = 50.0 \text{ mm}$). The oxygen

concentration in the gas flow was determined using a GS Oxygen Sensor KE-25 with an accuracy of $\pm 1\%$.

The kinetic regularity of the catalytic oxidation process was studied by changing the initial rate of mercaptide (C₃H₇S) oxidation, which was determined by using the Origin Software (Microcal LLC, Northampton, MA). The determination of the initial rate is based on the equation of the kinetic curve of mercaptide oxidation as described in the previous study (Hoang et al., 2021). The reaction measurement was calculated as the arithmetic mean of three parallel experiments. The relative error of the measurement varied between 1 and 5%.

3. Results and discussion

3.1. Characterization of the catalyst

OligoCat-Cu obtained is a black powder, completely insoluble in water and toluene, poorly soluble in acetone, and readily dissolvable in DMF and DMSO. Comparative analysis of X-ray powder diffraction pattern of the obtained oligoCat-Cu with those of compounds involved in the synthesis and its intermediate products revealed the complete absence of inorganic salts in the diffractograms of resulting oligomers. In addition, the diffractograms of each obtained oligomers also differed significantly (Fig. 2). Specifically, the diffractograms of metal oligopyrocatecholates were entirely different from that of individual oligopyrocatechol. While the intense peaks of the crystalline phase were weakly presented in the oligoCat-Na₂ diffractogram, oligoCat-Cu was a crystalline phase with a minimum amorphous component. Concerned about the possibility of the coexistence of several crystalline phases in the oligoCat-Cu sample, a series of attempts have been conducted to further purify the studied sample and to increase its crystallinity. The obtained outcome showed that no new additional crystalline phase was detected (see Supplemental Fig. S2). Furthermore, the result of comparing the diffraction pattern of oligoCat-Cu in the tablet form with that in the initial powder form once again confirmed this finding and indicated the invariability of the structural state of the investigated catalyst (see Supplemental Fig. S3). Another important finding obtained from X-ray fluorescence analysis was that the copper content in the oligoCat-Cu sample was close to 80%, and the remaining components were mainly represented by sodium (12%), potassium (1%), and sulfur (7%) (see Supplemental Fig. S4). In other words, the sodium ion of the oligoCat-Na₂ structure was almost completely substituted by copper ion in the synthetic process of oligoCat-Cu. All stated results help in confirming the formation of a homogeneous structure named oligoCat-Cu with the participation of both components consisting of the oligopyrocatechol and the corresponding metal.

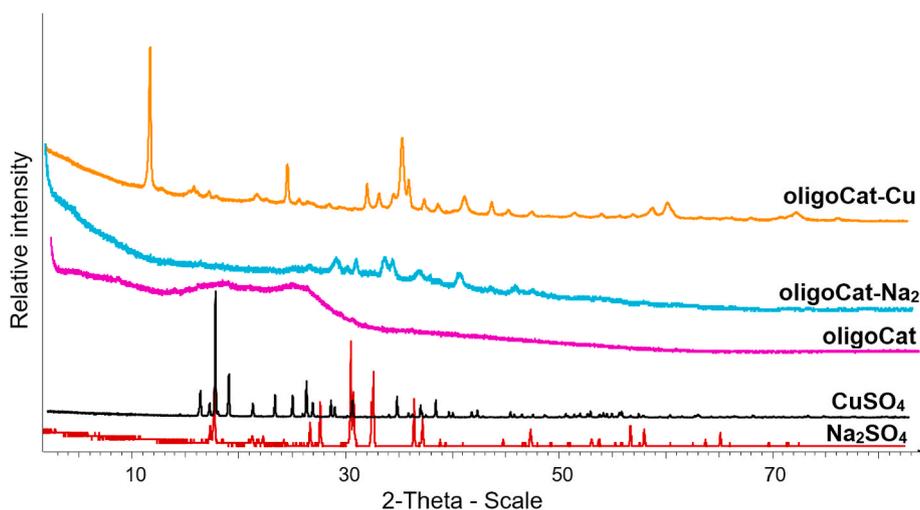


Fig. 2. Experimental powder diffractograms for the studied oligomers and inorganic salts.

3.2. Catalytic study

Although the obtained catalyst is entirely insoluble in water and even caustic soda solution, it is almost meaningless to use the oligoCat-Cu in powder form to catalyze the oxidative degradation of mercaptan in an aqueous alkaline solution. Using the powder form would increase the risk of losing a large amount of catalyst to the environment. Instead of treating contamination for the sake of environmental protection, a more toxic source of pollution is most likely created. Furthermore, in terms of financial issues, this would considerably increase the cost of waste treatment and the complexity of the operating system. To address this challenge, we have long developed and brought to market a heterogeneous catalytic system based on the dispersion of catalyst powder in a polymer matrix. More specifically, a certain amount of the catalytically active component was roll-mixed with the molten polymer at a high temperature (140–150 °C) until a uniform mass was obtained. The catalyst-polymer composite was then put into the mold and compacted at high pressure (10 kg cm⁻²). The obtained composite exhibits high stability (Nhi et al., 2013, 2014), and its catalytic activity can be maintained for up to 7 years under strongly alkaline conditions at temperatures up to 100 °C and pressures up to 7.0 kg cm⁻². Our product has optimized the catalytic oxidative degradation of sulfur-containing compounds and has been used reliably in many refineries and petrochemical plants around the world (<https://en.ahmadullins.com>). During the research and development process, since high mechanical properties

and strength reliability, high-density polyethylene (HDPE) has gradually replaced other polymers to become the mainstream in producing heterogeneous catalytic systems. Physicomechanical properties of HDPE were illustrated in Supplementary Table S1. One of our promising products widely used for the mercaptan removal process is the heterogeneous catalyst “KSM” consisting of 80 wt% HDPE and 20 wt% highly effective catalyst based on transition metal oxides and cobalt phthalocyanine derivative.

Based on existing achievements, we have dispersed the oligoCat-Cu in HDPE to assess the activity of the catalyst in the oxidative degradation of C₃H₈S in the aqueous caustic solution. In laboratory-scale, the composite oligoCat-Cu/HDPE was prepared in the form of a Rubik’s cube with an overall average size of 2 × 2 × 2 mm. Elemental analysis of the surface of oligoCat-Cu(20%)/HDPE using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) indicated that the average value of the atomic concentration of copper ions on the surface cube of oligoCat-Cu/HDPE was 0.17% (Fig. 3). It is possible to partially realize the uniform distribution of the oligoCat-Cu on the surface of the polymer matrix through the bright spot characteristic for copper atoms on the SEM image. The preliminary results (Table 1) showed that oligoCat-Cu/HDPE highly effectively catalyzed the oxidation of C₃H₈S absorbed into the liquid caustic soda. In a blank reaction with no catalyst added, C₃H₇S⁻ underwent slow oxidation with oxygen. With the presence of only a very small amount (1 wt%) of oligoCat-Cu contained in HDPE, the average oxidation rate had increased nearly

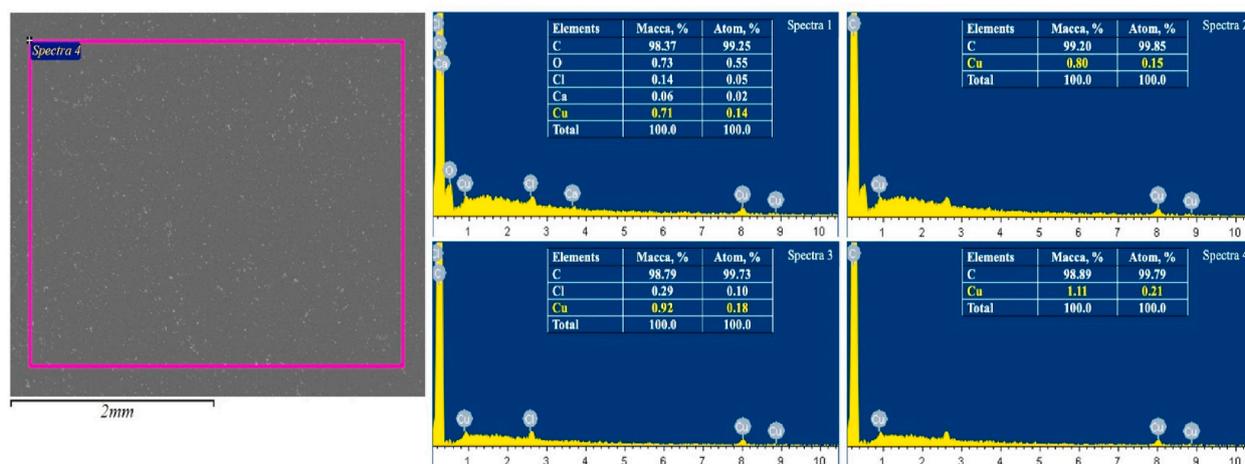


Fig. 3. SEM image and SEM-EDX analysis of oligoCat-Cu (20%)/HDPE surfaces.

Table 1

Aerobic oxidative degradation of isopropyl mercaptide $C_3H_7S^-$ in the presence and absence of oligoCat-Cu/HDPE based catalyst: Temperature – 50 °C, catalyst amount – 5 g, NaOH concentration – 10%.

Reaction run	Initial concentration of $C_3H_7S^-$, wt%	Without catalyst	oligoCat-Cu (1%)/HDPE	oligoCat-Cu (20%)/HDPE
		$C_3H_7S^-$ concentration after 60 min of oxidation, wt%		
1st run	1	0.829	0.525	0.131
2nd run	1	0.832	0.515	0.122
3rd run	1	0.830	0.530	0.130

3.0 times. This value has continuously risen to over 5.0 times when oligoCat-Cu content reached 20 wt%, corresponding to approximately 90% of mercaptide being oxidized within 60 min at 50 °C.

In addition to high catalytic activity, we are also interested in catalytic stability and reusability of oligo-Cu/HDPE, which are one of the extremely important properties of a catalyst determining its applicability in practice. The results obtained from the preliminary investigation (Table 1) have not assessed the stability and reusability of oligo-Cu/HDPE. This prompted us to conduct a series of continuous experiments for one working week to monitor the change of catalytic activity of oligo-Cu(20%)/HDPE in the aerobic oxidative degradation of $C_3H_7S^-$, and the results are summarized in Table 2. Not surprisingly, oligo-Cu(20%)/HDPE activity remains unchanged after thirty consecutive catalytic runs with a total duration of up to 30 h. Afterward, this catalyst was put into use during the kinetic mechanism study of mercaptan oxidation, the results of which will be discussed in the following sections. So far, its catalytic activity has not changed significantly. Thus, it can be partly confirmed that oligo-Cu/HDPE, like all our heterogeneous catalysts prepared by the above method, possesses high catalytic activity and stability in the aerobic catalytic oxidation of mercaptan.

Basic investigations mentioned above had demonstrated that oligoCat-Cu was highly effective as a catalyst for the oxidative degradation of mercaptan. However, applying this catalyst to the formulation of an alternative technique for mercaptan pollution control requires a detailed understanding of the dynamic behavior of the catalytic reaction process. Thus, the effect of various process variables such as initial concentration mercaptan, oxygen levels in the oxidizing gas stream, caustic concentration, catalyst content in polymer composite matrix, and reaction temperature was investigated.

Aerobic oxidation of isopropyl mercaptan in the presence of oligoCat-Cu based catalyst occurs at the interface between the phases of the dispersed system “heterogeneous catalyst – alkaline solution of mercaptan – oxygen”. The reaction limitation, therefore, is controlled not only by the mercaptide oxidation but also by the diffusion of reactants, in other words by the mass transfer resistance. To estimate the kinetics of this reaction, it is necessary to control the hydrodynamics/operational parameters of the batch reactor, such as the rotational speed of magnetic stirrer and gas supply rate, to achieve a maximum oxygen transport rate that overcomes any mass transfer limitations.

Accordingly, we evaluated the effect of stirring intensity on oxidative reaction rate by measuring the $C_3H_7S^-$ conversion at a fixed oxygen-flow

Table 2

Preservation of catalytic activity of oligo-Cu(20%)/HDPE in the aerobic oxidative degradation of isopropyl mercaptide $C_3H_7S^-$: Temperature – 50 °C, catalyst amount – 5 g, $[C_3H_7S^-]_0 = 1\%$, NaOH concentration – 10%.

Reaction time, min	0	30	60
Conversion of isopropyl mercaptide $C_3H_7S^-$, %			
Blank	0.00	7.80	16.80
1st run	0.00	47.90	86.80
10th run	0.00	57.50	87.20
20th run	0.00	48.60	87.00
30th run	0.00	51.00	87.50

rate of 270 h^{-1} . At the same time, we also assessed the effect of oxygen-supply rate on the oxidative reaction rate at a fixed rotational speed of magnetic stirrer. Both controlled experiments were carried out at 50 °C with the same initial concentration of $C_3H_7S^-$ (1%). The obtained results are set out in Fig. 4. It is evident from these results that the $C_3H_7S^-$ conversion increased with stirring intensity up to 1200 rpm. No significant variation was observed in the $C_3H_7S^-$ conversion as stirring intensity was further increased from 1200 rpm, indicating that the reaction is kinetically controlled. Therefore, a rotation rate of 1400 rpm was chosen for all subsequent experiments. At such a rotation frequency, the $C_3H_7S^-$ conversion is constant when the oxygen supply rate is above 270 h^{-1} . Therefore, to exclude the effect of mass transfer resistance on the chemical kinetics of the studied reaction, further experiments would be performed at a stirrer rotation speed of 1400 rpm and an oxygen supply rate of 300 h^{-1} .

It is significant to study the kinetic regularities as well as establish the intrinsic kinetic equation for the catalytic reaction of mercaptan oxidation in an aqueous caustic solution. To that end, the differential method with varying initial concentrations of reagents was adopted so that the order of the investigated reaction to reactants can be identified. In addition, the necessary hydrodynamic conditions to establish a kinetic regime during these experiments were also maintained.

It is evident from analyzing the kinetic curves of $C_3H_7S^-$ oxidation at its various initial concentrations (as shown in Fig. 5a) that the plot of the logarithms of these initial rates versus the logarithmic initial concentrations of reductant is a straight line with a slope of approximately 1. In other words, the investigated reaction follows the first-order kinetics in $C_3H_7S^-$. This finding can be firmly reached thanks to the employment of an integral method. Accordingly, the linearity of the logarithm of $[C_3H_7S^-]_t/[C_3H_7S^-]_0$ upon the time can be accepted as evidence of a first-order rate dependence on the reductant concentration (Fig. 5b). Similar first-order behavior in mercaptide was observed in many kinetics studies of mercaptan oxidation with or without catalyst in the homogeneous or heterogeneous system (Chauhan et al., 2017; Ganguly et al., 2012; Leung and Hoffmann, 1988; Motahari et al., 2020; Reid and Barat, 2015; Zhan et al., 2020).

Under otherwise uniform conditions, a series of experiments were performed to analyze the effect of the oxygen concentration on the mercaptide oxidation, in which the oxygen concentration in the oxidizing gas stream varied from 20 to 100%. It is seen that under the kinetic control, the plot of the logarithm of the initial oxidation rate versus the logarithm of initial oxygen concentration in the oxidizing gas

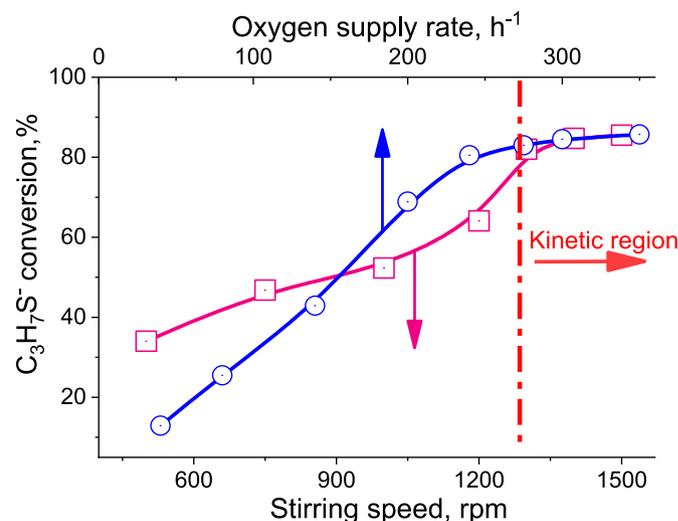


Fig. 4. The conversion rate of $C_3H_7S^-$ as a function of stirring speed (a) and oxygen supply rate: Temperature – 50 °C, catalyst amount – 5 g, $[C_3H_7S^-]_0 = 1\%$, NaOH concentration – 10%, reaction time – 60 min.

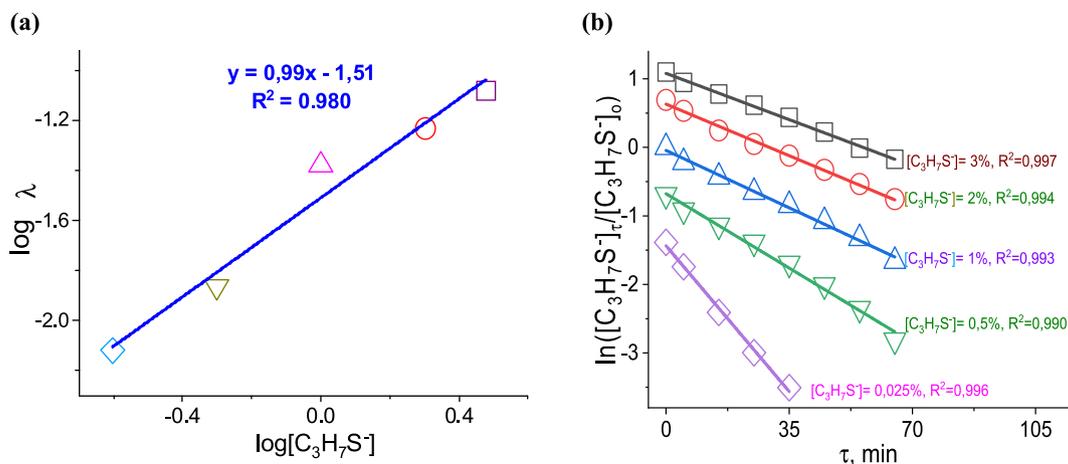


Fig. 5. The plot of logarithmic initial rate of $C_3H_7S^-$ oxidation against the logarithm of its initial concentrations (a), and the logarithm of $C_3H_7S^-$ concentrations during the course of the reaction (b): Temperature – 50 °C, catalyst amount – 5 g, NaOH concentration – 10%.

stream is a straight line with a slope of 0.5 (as shown in Fig. 6a). This observation indicated that the apparent reaction order in oxygen concentration was one-half.

Although it is obvious that increasing the catalyst amount improves the reaction rate, the investigation of the impact of catalyst amount on the catalytic reaction will help in shedding more light on the reaction mechanism. As described above, oligo-Cu (20%)/HDPE is a Rubik's cube with an overall average size of $2 \times 2 \times 2$ mm, and consequently, the area of one cube is 24 mm^2 . Meanwhile, 1 g of oligo-Cu (20%)/HDPE consists of about 65 cubes; in other words, the overall surface of 1 g of the catalyst is 1560 mm^2 . Thus, with 0.17% of atomic concentration of copper ions on the catalyst surface, the relative value of the average surface area of oligo-Cu in 1 g of oligo-Cu (20%)/HDPE is 2.65 mm^2 . Based on the linear dependence of the logarithmic initial rate of the mercaptide oxidation on the logarithm of catalytic surface area (Fig. 6a), the third-order of the reaction to the catalyst is established.

Thus, the overall kinetic equation for the reaction of aerobic catalytic oxidation of isopropyl mercaptide in the presence of oligo-Cu/HDPE can be represented as:

$$\nu = k \times [C_3H_7S^-]^1 \times [O_2]^{0.5} [\text{oligoCat} - Cu]^3 \quad (1)$$

where ν is the rate of catalytic oxidation of mercaptide, k is the rate

constant.

Since the oxidation reaction of $C_3H_7S^-$ was carried out under excess of both oxygen and catalyst, the reaction order can be attributed to pseudo-first to the mercaptide. Thus, the overall kinetic equation can be expressed in the simplified form:

$$\nu = k_{\text{eff}} \times [C_3H_7S^-] \quad (2)$$

The effective rate constant k_{eff} for the pseudo-first-order reaction was calculated from the plot of the linear dependence $\ln([C_3H_7S^-]_{\tau} / [C_3H_7S^-]_0)$ versus reaction time τ . As mentioned above, the reaction of catalytic oxidation of mercaptide in the presence of oligoCat-Cu/HDPE occurred at the interface, the reaction rate was nevertheless determined by the change in the volume concentration of reductant. The observed activation energy for the investigated reaction, therefore, refers to the apparent one. To estimate the apparent activation energy (E_a) of the aerobic catalytic oxidation of $C_3H_7S^-$, the alteration of the effective rate constant within the established temperature range for degradation of mercaptide under industrial conditions (30–70 °C) was studied at initial mercaptide concentration – 1%, oligoCat-Cu/HDPE amount – 5 g, oxygen concentration – 99.99% and alkaline concentration – 10%.

The apparent activation energy calculated according to the Arrhenius equation under the above condition equals $27.71 \pm 1.12 \text{ kJ mol}^{-1}$,

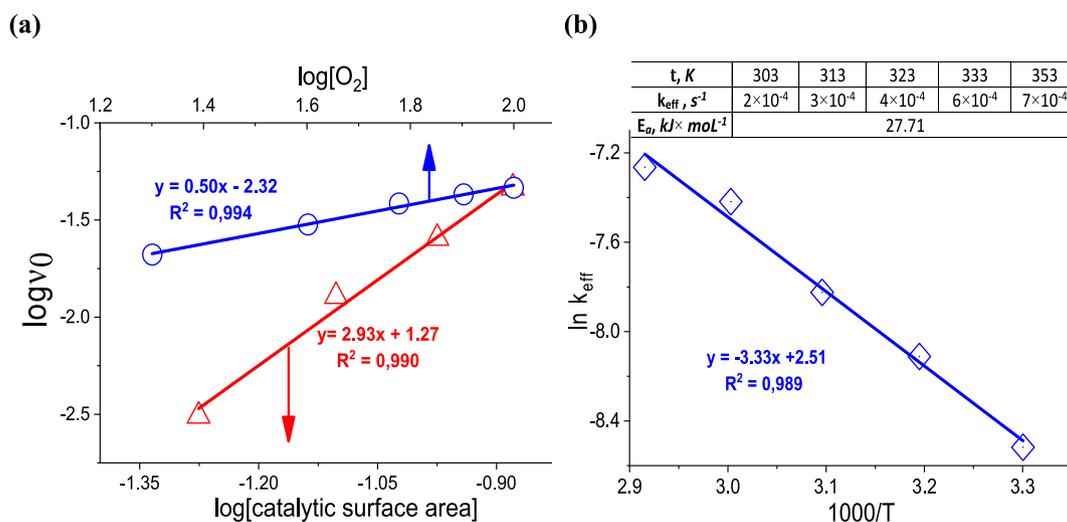


Fig. 6. Plots of the logarithmic initial rate of $C_3H_7S^-$ oxidation against the logarithm of initial concentrations of oxygen and the logarithm of catalytic surface area (a); The Arrhenius plot for $C_3H_7S^-$ oxidation in the presence of oligoCat-Cu/HDPE based catalyst (b): $[C_3H_7S^-]_0 = 1\%$, NaOH concentration – 10%, reaction time – 60 min.

and the pre-exponential factor in the Arrhenius equation at 50 °C is also determined to be $12.14 \pm 0.62 \text{ c}^{-1}$ (Fig. 6b). Therefore, the calculation equation for determining the pseudo-first-order reaction rate of the aerobic catalytic oxidation of $\text{C}_3\text{H}_7\text{S}^-$ in the presence of oligo-Cu/HDPE is described as follows:

$$\nu = 12.14 \times \exp\left(\frac{27710}{R T}\right) \times [\text{C}_3\text{H}_7\text{S}^-] \quad (3)$$

where R – the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T – the reaction temperature to Kelvin (K).

The effect of caustic strength and concentration on the rate of aerobic catalytic oxidation of isopropyl mercaptan in the presence of oligo-Cu/HDPE was also studied. The alkaline solution is essential for mercaptan oxidation since the reactive mercaptide ion is formed in the caustic phase. In this study, isopropyl mercaptan was sweetened in the presence of oligoCat-Cu/HDPE using 5%, 10%, 20%, 30% NaOH solutions. As shown in Fig. 7, the observed rate constants for the aerobic catalytic oxidation of $\text{C}_3\text{H}_7\text{S}^-$ decreased with the increase in the concentration of alkali. This phenomenon was best rationalized as being due to markedly lower solubility of oxygen in the stronger alkali (Schalenbach, 2018). Shown in Fig. 7 were double logarithmic plots of initial rates of $\text{C}_3\text{H}_7\text{S}^-$ oxidation as a function of alkali concentration. The slope of this linear function confirms that the mercaptide oxidation rate was inversely proportional to the first power of the alkali concentration. This rate law obtained from the kinetic study of $\text{C}_3\text{H}_7\text{S}^-$ oxidation can be used to design industrial reactors for the light oil sweetening process.

3.3. Catalytic mechanism

There have been studies to suggest the mechanism of the catalytic oxidation of mercaptan by oxygen in the caustic solution. Still, the most common mechanism so far was proposed by Wallace et al. (1964). They supposed that the base-catalyzed oxidation of mercaptan in the presence of an oxidation-reduction catalyst would occur by an anion-radical mechanism. Accordingly, after the ionization of mercaptan in alkaline solution has occurred, oxygen would react with metal cation by a one-electron transfer reaction to produce its next highest oxidation state and peroxide ion. The catalyst regeneration occurred by a one-electron transfer reaction between the oxidized cation and the mercaptide ion.

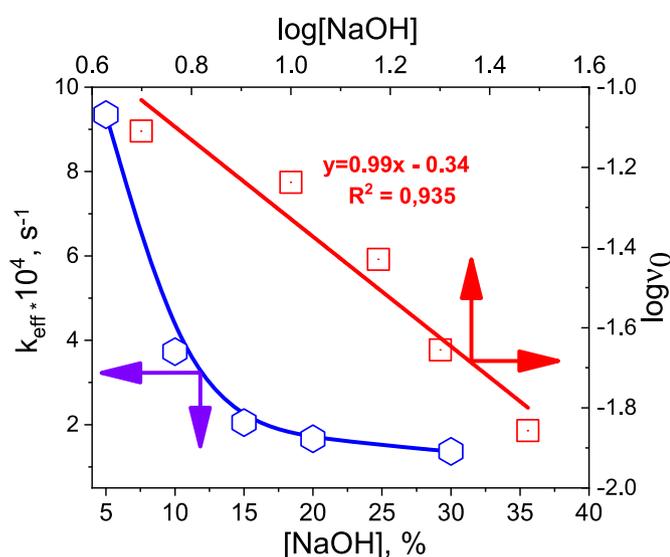


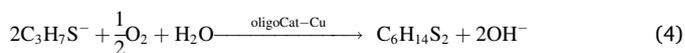
Fig. 7. The effective rate constant k_{eff} for $\text{C}_3\text{H}_7\text{S}^-$ oxidation as a function of NaOH concentration in the caustic solution, as well as the plot of logarithmic initial rate of $\text{C}_3\text{H}_7\text{S}^-$ oxidation against the logarithmic initial concentrations of NaOH: Temperature – 50 °C, catalyst amount – 5 g, $[\text{C}_3\text{H}_7\text{S}^-]_0 = 1\%$, reaction time – 60 min.

The resulting mercaptyl radicals dimerized, and the peroxide ion would be decomposed by water.

For the last twenty decades, an increasing number of experimental studies have suggested a ternary-complex mechanism for aerobic catalytic oxidation of mercaptan by metal phthalocyanine or its derivatives in the presence of caustic soda as cocatalyst. In this mechanism, the ordered ternary complex was formed when monomeric metal phthalocyanine bound with each of its two apical coordination sites, one with mercaptide ion and one with an oxygen molecule. According to electron spin resonance studies (Hoffmann and Hong, 1987; Jones et al., 1979), the formation of superoxide-like ternary metal complexes during the catalytic oxidation of sulfur-containing compounds was established. According to another aspect, mercaptide ion possesses a better electron-donating capacity and much higher polarizability than molecular oxygen. One question was whether mercaptide ion or oxygen molecule preferentially adsorbed on the central atom metal of catalyst. Therefore, the proposed complex mechanism could be classified into two schools. One assumed that oxygen would be preferentially adsorbed on the catalyst (Chauhan et al., 2003; Kotronarou et al., 1992; Leung and Hoffmann, 1988). Conversely, mercaptide ion was superior to oxygen molecule adsorbed on the catalyst (Chauhan et al., 2017; Reid and Barat, 2015; Scott et al., 2019). Recently, in the study of the kinetics of catalytic oxidation of sodium ethanethiolate, Zhan Y.Y. and co-workers (Zhan et al., 2020) by conducting in-situ UV-vis spectra analysis and density functional theory (DFT) calculations have proved that mercaptide ions in the alkaline solution were preferentially adsorbed on central cobalt atom of the CoSPc catalyst. One interesting observation from this study is that the charge of the central metal atom has not significantly changed after mercaptide ion or molecular oxygen are adsorbed on the catalyst. Nevertheless, only once the mercaptide ion and oxygen molecule are adsorbed together on the catalyst, the metal charge immediately becomes more remarkable, and a part of electrons is transferred from the metal to the oxygen molecule.

Based on these valuable findings, the suggested mechanistic pathway depicting aerobic oxidation of isopropyl mercaptan in the presence of oligoCat-Cu/HDPE-based catalyst is shown in Fig. 8. Accordingly, in the alkaline solution, the $\text{C}_3\text{H}_8\text{S}$ dissociates to an anion referred to as an isopropylate ($\text{C}_3\text{H}_7\text{S}^-$) as shown in Eq. (1). In Eq. (2), the resulting $\text{C}_3\text{H}_7\text{S}^-$ is adsorbed on oligo-Cu, forming a $\text{C}_3\text{H}_7\text{S}^- \dots \text{oligoCat-Cu(II)}$ complex in which the charge of central metal is almost unchanged. Oxygen adsorbed on $\text{C}_3\text{H}_7\text{S}^- \dots \text{oligoCat-Cu(II)}$ oxidizes the copper center to generate $\text{C}_3\text{H}_7\text{S}^- \dots \text{oligoCat-Cu(III)} \dots \text{O}_2^-$ complex as shown in Eq. (3). The isopropyl mercaptide radical dissociated from the complex dimerizes to form the disulfide and $\text{oligoCat-Cu(II)} \dots \text{O}_2^-$ (Eq. (4)) which reacts with water to desorb oxygen and regenerate the catalyst and hydroxyl ion as described in Eq. (5).

The overall reaction is presented as follows:



According to the proposed catalytic cycle described in Fig. 8, several elementary reactions can be considered as the rate-determining step such as the oxygen and mercaptide ion complexing with the catalyst (Eq. (2) and (3)), the subsequent electron-transfer steps (Eq. (4)), and the dissociation of the oxygen from the catalyst (Eq. 5). Nevertheless, it is seemingly that the subsequent electron-transfer step is probably to be the rate-limiting step since the order dependence of both oxygen and reductant concentrations on oxidation rate is less than that of catalyst amount. In addition, reductant and oxygen complexation with the catalyst as well as the dissociation of the oxygen from the catalyst will be fairly rapid ligand substitutions. The rate of ligand substitution for first-row transition metals is generally independent of the ligand nature. The calculated rates for each central metal ion are equivalent to their corresponding water-exchange rates. Hence, the rate of ligand substitution for metal ions will be roughly equivalent to its water exchange rate. While the water-exchange rate for Cu^{2+} is $4.4 \times 10^9 \text{ s}^{-1}$ (Helm and

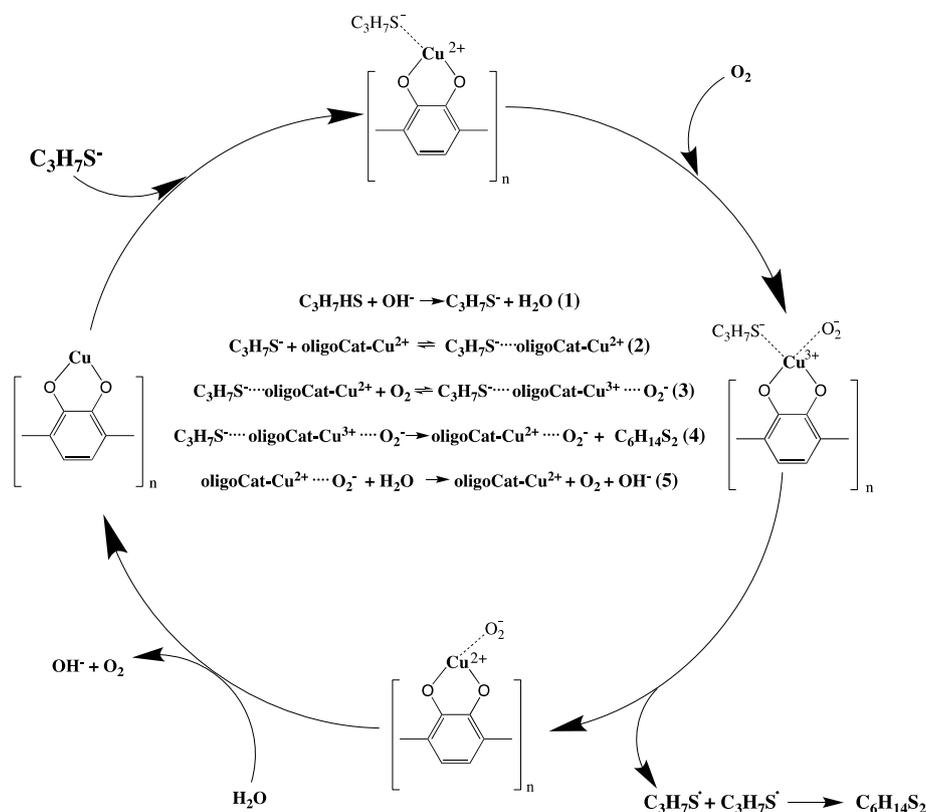


Fig. 8. The catalytic cycle of aerobic oxidation of isopropyl mercaptan in the aqueous caustic solution.

Merbach, 2002), the characteristic rate constant for reductant complexation and oxygen coordination of the central copper ion in oligoCat-Cu/HDPE is on the order of 10^4 . This value is five orders of magnitude larger than the rate constants obtained by us. Thus, it can be confirmed that the subsequent electron transfer is the rate-determining step of aerobic oxidation of mercaptide in the presence of oligo-Cu/HDPE-based catalyst. This important conclusion may help us to explain an interesting finding in the kinetic study section as to why, compared with the concentrations of oxygen and reductant, the catalyst amount greatly affects the rate reaction of aerobic catalytic oxidation of isopropyl mercaptan in the caustic solution.

4. Conclusion

In summary, we have developed a simple and highly efficient synthetic route to prepare a novel catalyst based on bivalent transition metal oligopyrocatecholate for aerobic catalytic oxidation of mercaptan. The kinetics of isopropyl mercaptide oxidation in the presence of a catalyst based on copper oligopyrocatecholate dispersed in the polymer matrix has been presented as a pseudo-first-order reaction to mercaptide. In addition, the reaction rate was directly proportional to the third power of catalytic surface area and the half-power to the oxygen concentration as well as inversely proportional to the first power of the alkali concentration. Importantly, this rate law for isopropyl mercaptide oxidation can be used to design industrial reactors for the light oil sweetening process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2021.112171>.

Credit author statement

R.M. Akhmadullin: Supervision, Methodology, Conceptualization, Data curation, Reviewing and Final revisions. A.T. Gubaidullin: Conceptualization, Methodology, Kh. E. Kharlampidi: Conceptualization, Methodology S.R. Kurbankulov: Investigation, Data curation, Formal analysis. T.F. Nigmatullin: Investigation, R.F. Khamidullin: Conceptualization, A.G. Akhmadullina: Methodology, Conceptualization. M.U. Dao: Reviewing, Methodology, Software, Visualization, Formal analysis. Y. Vasseghian: Reviewing, Software. H.Y. Hoang: Methodology, Conceptualization, Data curation, Software, Formal analysis, Writing - Original draft - Reviewing- Editing, Supervision.

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