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Synthesis, characterization and catalytic activity of cobalt phthalocyanine tetrasulphonamide in sweetening of LPG

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ABSTRACT

Cobalt phthalocyanine tetrasulphonamide was synthesized by reacting cobalt phthalocyanine with chlorosulphonic acid at 130–135 °C followed by addition of thionyl chloride to convert free sulphonic acid to sulphonyl chloride and subsequently amidation with ammonia. It was isolated by acidifying the reaction mixture with hydrochloric acid followed by filtration. It was characterized by elemental IR and FAB mass spectral analysis. The activity of cobalt phthalocyanine tetrasulphonamide catalyst for extractive sweetening of LPG was evaluated by studying mercaptide oxidation using ethyl mercaptan as model sulfur compound in glass column. The stability of the catalyst was evaluated by studying liquid–liquid sweetening in a batch reactor using hexane thiol as a model compound and petroleum ether as an inert solvent. The performance of this catalyst with respect to activity and stability was found better than the commercial catalyst being used currently in the refineries. Commercial trial run of this catalyst has been successfully conducted for 4 months in FCC LPG Merox unit of Bharat Petroleum Corporation Limited (BPCL), Mumbai and the performance was found better than commercial catalyst. Another trial run of the catalyst has been conducted in one of the LPG Merox units at Reliance Industries Limited (RIL), Jamnagar for 8 months and the performance has been found to be excellent with less catalyst consumption than commercial catalyst.

1. Introduction

The presence of mercaptans in the petroleum products like LPG, naphtha, gasoline, kerosene, ATF etc. is highly undesirable due to their foul odour and highly corrosive nature. Although there are several processes known for the removal of mercaptans from petroleum products, the most common practice is to oxidize the mercaptans present to less deleterious disulphides with air in the presence of a catalyst. Generally, the lower mercaptans present in LPG, pentanes, light straight run naphtha (LSRN) and light thermally cracked naphtha are first extracted by alkali solution and then oxidized to disulphides with air in the presence of a catalyst. The disulphides, being insoluble in alkali solution are separated out from the top and the regenerated alkali is reused for extraction. In the liquid–liquid sweetening the lower mercaptans are present in petroleum products like pentanes, LSRN, cracked naphtha etc. are converted to disulphides by direct oxidation with air in the presence of alkali solution and catalyst. The higher molecular weight mercaptans present in petroleum products like heavy naphtha, FCC gasoline, ATF and kerosene are oxidized to disulphides with air in a fixed bed reactor containing catalyst impregnated on a suitable support like activated carbon.

Phthalocyanines of the metals like cobalt, iron, manganese, molybdenum and vanadium catalyze the oxidation of mercaptans to disulphides in alkaline medium [1]. Among these cobalt and vanadium phthalocyanines are preferred. As the metal phthalocyanines are not soluble in aqueous medium, for improved catalytic activity their derivatives like sulphonated and carboxylated metal phthalocyanines are used as catalysts for sweetening of petroleum fractions. The use of cobalt phthalocyanine (CoPc) monosulphonate as the catalyst in the fixed bed sweetening of various petroleum products and cobalt phthalocyanine disulphonate [2] tetrasulphonate [3] and the mixture thereof [4] as catalysts for liquid–liquid sweetening/alkali regeneration in mercaptan extraction of light petroleum distillates have been reported. The use of phenoxy substituted cobalt phthalocyanine as sweetening catalyst [5], cobalt and vanadium chelates of 2,9,16,23-tetrakis(3,4-dicarboxybenzoyl)phthalocyanine as effective catalyst for homogeneous mercaptan oxidation [6,7] and cobalt/vanadium chelates of tetrapyridinoporphyrazine as active catalysts for sweetening of sour petroleum distillates [8] have also been reported.

Cobalt phthalocyanine disulphonate a commonly used catalyst in sweetening of LPG and light petroleum fractions by liquid–liquid

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mercaptan extraction and alkali regeneration is extremely dusty in the dry fine powder form and causes handling problem. To overcome this problem cobalt phthalocyanine disulphonate is admixed with water and commonly used as slurry. However, with insufficient mixing the cobalt phthalocyanine disulphonate precipitates out from the slurry. Moreover, even if the slurry is mixed sufficiently, it retains the cobalt phthalocyanine disulphonate in suspension for a particular length of time only, beyond which the slurry becomes extremely viscous and may form gel, making it very difficult to remove the material from packaging. Cobalt phthalocyanine tetrasulphonate, on the other hand, is highly soluble in water and its use can eliminate precipitation and gel forming problems associated with the use of cobalt phthalocyanine disulphonate. However, it is reported that cobalt phthalocyanine tetrasulphonate has lower catalytic activity than cobalt phthalocyanine disulphonate [9].

During our investigations on development of new superior sweetening catalysts for extractive sweetening of LPG, our attention was particularly drawn by amide group, which has a peculiar property of increasing the solubility of organic compounds in aqueous alkaline solution. The essential requirement of the metal phthalocyanine sweetening catalysts for LPG is their high solubility in aqueous alkaline solution. Therefore, the use of cobalt phthalocyanine sulphonamides (Fig. 1) was explored as a new sweetening catalyst for extractive sweetening of LPG.

In this paper we describe synthesis, characterization and evaluation of catalytic activity of cobalt phthalocyanine tetrasulphonamide catalyst (IIP Cat) in extractive sweetening of LPG and its stability for liquid–liquid sweetening of synthetic feed consisting of hexane thiol ($C_6H_{13}SH$) in petroleum ether (60–80 °C). The performance of this catalyst in the commercial plant trial run is also discussed.

2. Experimental

Cobalt phthalocyanine used was obtained from M/s Lona Industries Ltd. Mumbai. All the chemicals and solvents used were LR grade and purchased from standard chemicals suppliers. Infrared (IR) spectra of the catalyst were recorded on PerkinElmer 1760X FTIR spectrophotometer, in KBr pellet qualitatively. Fast atom bombardment (FAB) mass spectra of the catalyst were recorded on a JEOL SX 102/DA 6000 mass spectrometer/data system using argon/xenon (6 kV,10 mA) as FAB gas in *m*-nitro benzyl alcohol matrix at RSIC, CDRI Lucknow.

For estimation of mercaptan content in feed and product by potentiometric titration method, an automatic titration unit Mettler DL 50 was used.

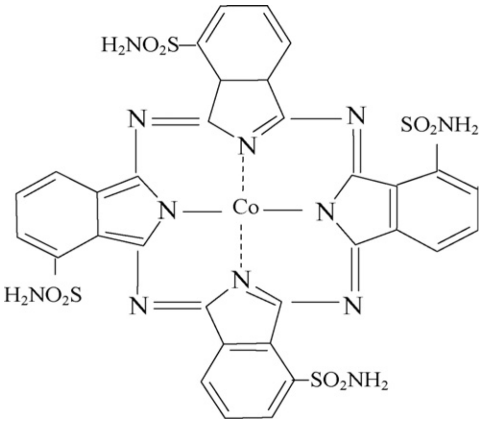

Fig. 1. Structure of cobalt phthalocyanine tetrasulphonamide.

2.1. Preparation of cobalt phthalocyanine tetrasulphonamide

Cobalt phthalocyanine tetrasulphonamide was prepared by the following procedure [10,11]. In a typical experiment cobalt phthalocyanine was slowly added with stirring to 10-fold excess by weight of chlorosulphonic acid. The mixture was then slowly heated in steps to 130 °C and maintained at 130–135 °C for 4 h. Reaction mixture was than cooled to below 60 °C and little more than two-fold excess by weight of thionyl chloride were slowly added. The whole contents were heated to 79 °C and maintained at this temperature for 1 h. The reaction mixture was then cooled to room temperature and slowly added to crushed ice keeping the temperature preferably below 5 °C. The precipitated cobalt phthalocyanine tetrasulphonyl chloride was filtered and washed thoroughly with cold water. The wet sulphonyl chloride cake thus obtained was dispersed in 30 parts by weight excess of ice water and six parts excess of methanol. The mixture was stirred at 5–8 °C and ammonia gas was passed till the mixture become fairly alkaline. Catalytic amount of pyridine and sodium hydroxide were then added and reaction mixture stirred at room temperature for 40 min. The reaction mixture was then heated to 80 °C, and after maintaining at this temperature for 1 h, cooled to room temperature and poured over a mixture of ice and concentrated HCl keeping pH fairly acidic. The precipitated cobalt phthalocyanine tetrasulphonamide was filtered and washed thoroughly with cold water and dried in vacuum oven to yield cobalt phthalocyanine tetrasulphonamide powder in almost quantitative yield.

Liquid form of the catalyst was prepared by dissolving the powder form of the catalyst in 2–3 wt% aqueous sodium hydroxide solution with the aid of dispersing agents.

2.2. Activity of the catalyst for LPG sweetening

The semi-batch bubble column type reactor made up of glass (900 mm long × 40 mm dia) fitted with a sintered glass sheet for uniformly distributing the air flow and jacketed to maintain the desired reaction temperature by circulating water from a thermostatic bath was used for catalytic activity test. The flow rate of air introduced from the bottom of the column was measured by a calibrated manometer and cross-checked by a wet gas flow meter. Required amount of ethyl mercaptan was added to 230 ml 14% aqueous sodium hydroxide solution filled in the glass column and purging of nitrogen through NaOH solution was started in an up flow mode to remove dissolved oxygen and maintain an inert atmosphere. Calculated amount of cobalt phthalocyanine tetrasulphonamide/commercial catalysts required for maintaining a concentration of 200 ppmw in the reaction mixture was dissolved in 4–5 ml of 4% aqueous NaOH solution and added to the ethyl mercaptan solution in NaOH through the septum. The gas flow was then quickly changed from nitrogen to air with the help of a three-way glass valve. The colour of the reaction mixture changed from dark greenish black (initially) to blue indicating the completion of the reaction. The mercaptide sulfur concentration in samples collected at different times was analyzed by potentiometric titration method UOP: 163-89.

2.3. Stability of catalyst

The feed was prepared by dissolving calculated amount of hexane thiol in petroleum ether and kept in a feed vessel with an outlet valve. A sample of the feed was analyzed by potentiometric titration method UOP: 163-89 to estimate mercaptan content. For maintaining desired level of catalyst concentration in reaction mixture, calculated amount of cobalt phthalocyanine tetrasulphonamide/commercial catalyst was dissolved in 7% aqueous NaOH solution (20 ml) and taken in a three necked round bottomed flask fitted with gas inlet tube, condenser and mechanical stirrer. Feed (100 ml) was then added from feed vessel to the flask, stirring and air flow rate were started simultaneously and continued for 10 min. Initially the colour of reaction mixture became greenish black and turned to blue at the end indicating almost complete conversion of thiol to disulphide. After allowing little time for separation of caustic the petroleum ether layer was taken out from the flask. Again 100 ml fresh feed was added to the used catalyst solution in the flask. The same procedure was repeated several times by contacting same catalyst solution with fresh feed till the product mercaptan content was found to increase. Initially mercaptan content was checked by qualitative Doctor Test and later estimated quantitatively by same method UOP: 163-89 after the Doctor Test became positive.

3. Results and discussion

3.1. LPG sweetening

Sweetening of LPG involves extraction of the mercaptan present in it by aqueous alkaline solution followed by their oxidation to disulphide with air in presence of metal chelate like cobalt phthalocyanine (Co^{2+}) as catalyst. The mechanism of the reaction as proposed by Wallace et al. [12] is shown in Scheme 1.

In commercial sweetening process the catalyst is injected to 12–14% aqueous sodium hydroxide solution, which kept on circulating in the system consisting of extractor, oxidizer and disulphide separator.

As the metal phthalocyanines are normally not soluble in aqueous alkaline solution, their sulphonated or carboxylated derivatives are used as sweetening catalysts. For sweetening of LPG, whereby the presence of sulphonamide group not only makes cobalt phthalocyanine highly soluble in aqueous sodium hydroxide but also increases its catalytic activity probably due to change of redox potential of cobalt.

3.2. Preparation and characterization of catalyst

The essential requirement of the metal phthalocyanine based LPG sweetening catalyst is their high solubility in aqueous sodium hydroxide solution along with catalytic activity for oxidation of mercaptide to disulphide. Although the uses of several sulphonated, carboxylated and other derivatives of metal phthalocyanine as LPG sweetening catalysts are reported in literature, but cobalt phthalocyanine disulphonate is most commonly used. Here the use of cobalt phthalocyanine tetrasulphonamide has been described as a new catalyst.

Cobalt phthalocyanine tetrasulphonamide was prepared by chlorosulphonation of cobalt phthalocyanine with chlorosulphonic acid followed by amidation with ammonia. During chlorosulphonation, cobalt phthalocyanine first reacts with 4 mol of chlorosulphonic acid to give cobalt phthalocyanine tetrasulphonic acid, which subsequently reacts with excess of chlorosulphonic acid to yield cobalt phthalocyanine tetrasulphonyl tetrachloride. However, even with large excess of chlorosulphonic acid, all the sulphonic acid groups attached to cobalt phthalocyanine are not converted to sulphonyl chloride groups. Therefore, after chlorosulphonation the product was treated with thionyl chloride to ensure the complete conversion of sulphonic acid groups to sulphonyl chloride and get maximum yields of cobalt phthalocyanine tetrasulphonyl chloride. The reaction sequences for the formation of cobalt phthalocyanine tetrasulphonamide are shown in Scheme 2.

$$
\begin{aligned}
&\mathrm{RSH + OH^-} && \rightleftarrows && \mathrm{RS^- + H_2O}\\
&\mathrm{2Co^{2+} + O_2} && \rightleftarrows && \mathrm{2Co^{3+} + O_2^{2-}}\\
&\mathrm{2RS^- + Co^{3+}} && \longrightarrow && \mathrm{Co^{2+} + RS^*}\\
&\mathrm{2RS^*} && \longrightarrow && \mathrm{RSSR}\\
&\mathrm{O_2^{2-} + H_2O} && \longrightarrow && \mathrm{2OH^- + ½\,O_2}
\end{aligned}
$$

The overall reaction

$$\mathrm{2\,RSH + ½\,O_2 \longrightarrow RSSR + H_2O}$$

Scheme 1. Reaction mechanism.

By employing controlled conditions, 92–95% yield of cobalt phthalocyanine tetrasulphonamide has been obtained starting with cobalt phthalocyanine. The intermediate product cobalt phthalocyanine tetrasulphonyl chloride was found to be unstable at room temperature and was converted into cobalt phthalocyanine tetrasulphonamide immediately after its isolation. Experiments were carried out both with and without thionyl chloride and it was observed that addition of thionyl chloride after chlorosulphonation with chlorosulphonic acid showed marked improvement in the yield as well as in the stability of the catalyst.

Cobalt phthalocyanine tetrasulphonamide was characterized through elemental analysis as well as spectroscopic techniques. Molecular formula is $C_{32}H_{20}N_{12}S_4O_8Co$, elemental analysis, calculated (C, 43.29; H, 2.27; S, 14.45; Co, 6.64) and found (C, 41.62; H, 2.34; S, 13.02; Co, 6.36).

IR spectra showed major peaks at 3399, 3152, 1627, 1521, 1400, 1327, 1253, 1160, 1110, 1036, 926, 751 and 571 cm^{-1}. The broad peaks at 3399 and 3152 cm^{-1} were assigned to N–H stretching vibrations and were found to be broad probably due to the presence of moisture in the sample. The intense peaks at 1400, 1521 and 1627 cm^{-1} were assigned to aromatic C═C stretching vibrations. The intense peaks at 1160 and 1327 cm^{-1} were assigned to S═O stretching vibrations of sulphonamide group. The medium intensity peaks at 751 was assigned to aromatic C–H bending vibrations. An overlay of the IR spectra of the catalyst and cobalt phthalocyanine clearly indicates the presence of amino group (3399, 3152 cm^{-1}) and S═O of sulphonamide group (1160, 1327 cm^{-1}).

FAB mass spectra showed most prominent peak in the high mass range at 888 (molecular weight corresponding to molecular formula $C_{32}H_{20}N_{12}S_4O_8Co$), indicating the major product to be

$$
\begin{aligned}
&\mathrm{CoPc + 4ClSO_3H \longrightarrow CoPc(SO_3H)_4 + 4HCl}\\
&\mathrm{CoPc(SO_3H)_4 + nClSO_3H \longrightarrow CoPc(SO_2Cl)_n(SO_3H)_{4-n} + nH_2SO_4}\\
&\mathrm{CoPc(SO_2Cl)_n(SO_3H)_{4-n} + (4-n)SOCl_2 \longrightarrow CoPc(SO_2Cl)_4 + (4-n)SO_2 + (4-n)HCl}\\
&\mathrm{CoPc(SO_2Cl)_4 + 4NH_3 \longrightarrow CoPc(SO_2NH_2)_4 + 4HCl}
\end{aligned}
$$

CoPc : cobalt phthalocyanine

Scheme 2. Reaction sequence for preparation of cobalt phthalocyanine tetrasulphonamide.

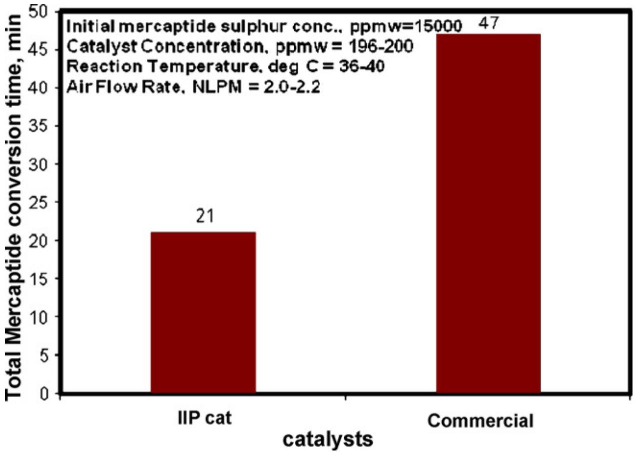

Fig. 2. Comparison of catalytic activities for mercaptide oxidation in terms of total conversion time.

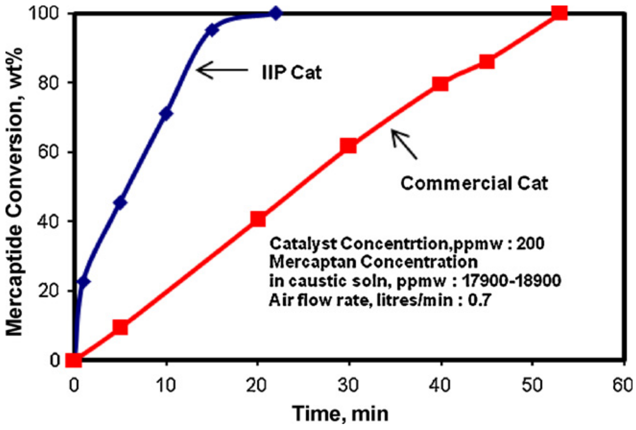

Fig. 3. Comparison of mercaptide conversion rate with different sweetening catalysts.

cobalt phthalocyanine tetrasulphonamide. The peaks at *m*/*a* 808 and 728 indicated the presence of small amounts of cobalt phthalocyanine trisulphonamide and cobalt phthalocyanine disulphonamide.

3.3. Activity and stability of catalyst

As the catalyst plays role in enhancing mercaptide oxidation rate in the oxidizer, activity of cobalt phthalocyanine tetrasulphonamide was evaluated by studying mercaptide oxidation reaction (caustic regeneration) using ethyl mercaptan as model compound. Experiments were carried out by using 15000 ppmw mercaptide sulfur content in caustic feed as this corresponds to very high RSH content of 750–1000 ppmw in LPG feed depending upon caustic circulation to feed rate ratio. Activity of cobalt phthalocyanine tetrasulphonamide catalyst (IIP Cat) was compared with commercial catalyst under similar conditions.

Time required for total mercaptide conversion to disulphide, i.e., caustic regeneration were measured for this catalyst as well as commercial catalyst under similar conditions. The typical comparative results obtained are presented in Fig. 2 and show that total conversion time for IIP Cat is much lesser than that of commercial catalyst under similar conditions. It is evident from these results that IIP Cat is more active than commercial catalyst. The data obtained on the percent conversion of ethyl mercaptide to ethyl disulphide at different time intervals for both IIP Cat and commercial catalysts are shown in Fig. 3. Again it is evident that conversion rate for IIP Cat is more than the commercial one. These results clearly established the higher catalytic activity of IIP Cat in comparison to commercial sweetening catalyst for ethyl mercaptide oxidation to ethyl disulphide.

Table 1
Comparison of stability of IIP Cat with commercial catalyst

Cumulative volume of feed processed (l)	Mercaptan concentration in product (ppmw)	
	IIP Cat	Commercial catalyst
0.5	<5	<5
1.0	<5	<5
1.5	<5	<5
2.0	<5	<5
2.5	<5	<5
3.0	<5	<5
3.5	<5	<5
4.0	<5	<5
4.5	<5	<5
4.6	<5	<5
4.7	<5	<5
4.8	<5	<5
4.9	<5	<5
5.0	<5	<5
5.1	<5	<5
5.2	<5	<5
5.3	<5	<5
5.4	<5	<5
5.5	<5	<5
5.6	<5	<5
5.7	7.8	<5
5.8	8.0	9.0
5.9	11.7	13.0
6.0	13.0	19.5

Concentration of mercaptan in feed, ppmw: 755, catalyst concentration (feed basis), ppmw: 89.5, reaction time, min: 10, air flow rate, NLPM: 1.23, reaction temperature, °C: ambient.

Stability of cobalt phthalocyanine tetrasulphonamide catalyst vis-a-vis commercial one was evaluated by measuring cumulative volume of feed treated repeatedly with same quantity of catalyst maintaining same conditions for both the catalysts. For this purpose, experiments were conducted by using petroleum ether as an inert base and hexane thiol as a model compound. Hexane thiol was chosen as model sulphur compound because it is relatively more difficult to oxidize this to disulphide than ethane thiol. The experiments on liquid–liquid sweetening for both cobalt phthalocyanine tetrasulphonamide and commercial catalyst were carried out using feed having almost same mercaptan concentration at same catalyst concentration, air flow rate and reaction time. The typical results obtained on stability test by liquid–liquid sweetening of synthetic feed using IIP Cat and commercial catalyst are presented in Table 1. These results show that the conversion has started decreasing after processing 5.7 l of feed for both the catalysts. This shows that deactivation rate is almost similar for both the catalysts and therefore it can be concluded that both the catalysts have equivalent stability.

4. Commercial plant trial run

Commercial trial run of the cobalt phthalocyanine tetrasulphonamide catalyst was successfully undertaken in one of the FCC LPG Merox units of Bharat Petroleum Corporation Limited (BPCL), Mumbai for 4 months and the catalyst showed better performance than the commercial catalyst. Another commercial trial run of this catalyst for 8 months has just completed in one of the LPG Merox units of Reliance Industries Limited (RIL), Jamnagar and the performance has been found to be excellent with less catalyst consumption than the commercial one.

5. Conclusion

Cobalt phthalocyanine tetrasulphonamide catalyst prepared by chlorosulphonation of cobalt phthalocyanine with chlorosulphonic acid followed by amidation with ammonia has been found a potential catalyst for extractive sweetening of LPG. Laboratory evaluations have shown that while its activity is better than the commercial catalyst currently being used in the Indian refineries, its stability is equivalent. Trial runs conducted at BPCL, Mumbai and RIL refinery, Jamnagar have established the commercial potential of this catalyst for LPG sweetening.

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