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

Gautam Das *, Bir Sain *, Sunil Kumar, M.O. Garg, G. Murali Dhar

Indian Institute of Petroleum, Dehradun 248005, India

ARTICLE INFO

Article history:
Available online 4 June 2008

Keywords:
Cobalt phthalocyanine
Cobalt phthalocyanine tetrasulphonamide
LPG
Sweetening
Mercaptan
Oxidation
IIP

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.

© 2008 Elsevier B.V. All rights reserved.

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 (CoPe) 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 phenoxyl substituted cobalt phthalocyanine as sweetening catalyst [5], cobalt and vanadium chelates of 2,9,16,23-tetraakis(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
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 tetrasulphonamide 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 (IP Cat) in extractive sweetening of LPG and its stability for liquid-liquid sweetening of synthetic feed consisting of hexane thiol (C6HnSH) 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 anisidine (900 mm long x 40 mm dia) fitted with a sintered glass sheet for maintaining 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 (Co2+) 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 tetrasulphonamide, which subsequently reacts with excess of chlorosulphonic acid to yield cobalt phthalocyanine tetrachlorotetrasulphonamide.

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 tetrasulphonamide. The reaction sequences for the formation of cobalt phthalocyanine tetrasulphonamide are shown in Scheme 2.

By employing controlled conditions, 92-95% yield of cobalt phthalocyanine tetrasulphonamide has been obtained starting with cobalt phthalocyanine. The intermediate product cobalt phthalocyanine tetrasulphonamide 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_{4}O_{6}Co, 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=O and C=O 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_{4}O_{6}Co), indicating the major product to be cobalt phthalocyanine tetrasulphonamide.
obtained on the percent conversion of ethyl mercaptide to ethyl disulphide at different time intervals for both liP Cat and commercial catalyst. The data shows that liP Cat is more active than commercial catalyst. The data suggests that conversion time for liP Cat is much lesser than that of commercial catalyst. It is evident from these results that liP Cat is more active than commercial catalyst. The typical comparative results obtained are presented in Table 1. These results show that the conversion rate for liP Cat is more than the commercial one. These results clearly established the higher catalytic activity of liP Cat in comparison to commercial sweetening catalyst for ethyl mercaptide oxidation to ethyl disulphide.

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 liP Cat and commercial catalyst are shown in Fig. 3. Again it is evident that conversion rate for liP Cat is more than the commercial one. These results clearly established the higher catalytic activity of liP Cat in comparison to commercial sweetening catalyst for ethyl mercaptide oxidation to ethyl disulphide.

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 (liP 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 liP Cat is much lesser than that of commercial catalyst under similar conditions. It is evident from these results that liP 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 liP Cat and commercial catalysts are shown in Fig. 3. Again it is evident that conversion rate for liP Cat is more than the commercial one. These results clearly established the higher catalytic activity of liP Cat in comparison to commercial sweetening catalyst for ethyl mercaptide oxidation to ethyl disulphide.

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.

Acknowledgements

The authors are grateful to Bharat Petroleum Corporation Limited, Mumbai for financial support and conducting trial run of the catalyst in their refinery. Authors are also highly thankful to Reliance Industries Limited, for performance evaluation of the indigenously developed catalyst in their commercial plant.

References