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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.

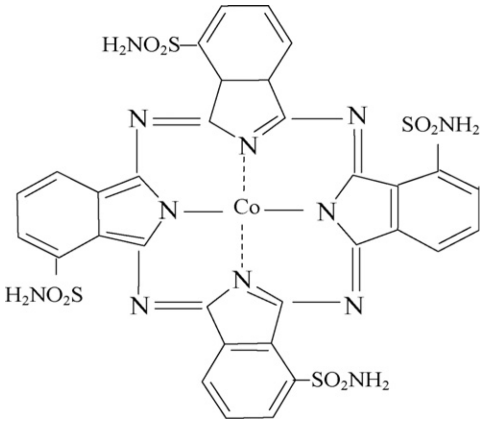

Fig. 1. Structure of cobalt phthalocyanine tetrasulphonamide.

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