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Catalysis Today 75 (2002) 113–117

CATALYSIS TODAY

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Oxidation of mercaptans in light oil sweetening by cobalt(II) phthalocyanine–hydrotalcite catalysts

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Abstract

Three Mg–Al hydrotalcites containing cobalt(II) phthalocyanine were prepared by direct synthesis, anion exchange and structure reconstruction. Differences in physicochemical properties and mechanical resistance were observed. The results of the mercaptan oxidation reaction were compared to those obtained with an industrial non-basic impregnated active charcoal. An important activity difference in favor of the prepared catalysts was obtained, confirming that the adequate tuning of basic and oxidant properties lead to a promising catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mg–Al hydrotalcite; Co(II) phthalocyanine; Mercaptan oxidation

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1. Introduction

Mercaptans are important impurities distributed among petroleum products. They cause foul odor, deterioration of additives in finished products and are corrosive [1]. Therefore, it is necessary to remove them by a conversion into innocuous disulfides. Such industrial process is usually referred to as “sweetening”. Mercaptans are oxidized to disulfides by air under caustic condition and in the presence of cobalt(II) phthalocyanine catalyst [1].

The aim of this work is to convert unwanted mercaptans into disulfides by contact of the petroleum cut with a bifunctional solid, avoiding then the consumption of a non-easily regenerated caustic solution. Many catalysts have been studied to substitute liquid bases by solids as zeolites [2], alumina [3,4], sepiolite [5] and hydrotalcites [6,7]. Hydrotalcites are the subject of this investigation. They are layered double hydroxides with the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A_{x/n}{}^{n-}]\cdot mH_2O$. The host layers are charged positively by replacement of divalent metal cations usually Mg^{2+} with trivalent ones generally Al^{3+}. The positive charge is compensated by anions occupying the interlamellar space [8,9]. Anions of any nature like simple anions, organic anions and metal complexes can be intercalated between the layers [9–14]. Incorporation of metal phthalocyanine complexes into the intergallery of hydrotalcite is the subject of many interest owing to their advantageous catalytic properties especially in oxidation reaction [15–18]. These catalysts could be prepared by different methods: direct synthesis (DS) [18,19], anion exchange (AE) [20] and structure reconstruction (SR) [21]. Carrado et al. [19] have intercalated Cu(II) phthalocyanine tetrasulfonate into the gallery of Mg–Al hydrotalcite through AE and DS. Kannan et al. [18] have intercalated the identical complex into the gallery of Mg–Al hydrotalcite by DS and

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PII: S0920-5861(02)00051-2

obtained a different orientation of the anion in the interlamellar space. Pinnavaia and coworkers [21] have tested Co(II) phthalocyanine, intercalated in Mg–Al hydrotalcite through SR, as catalyst in air oxidation of thiols at alkaline pH (9.25). This intercalated Co(II) complex was twice active than is the homogenous complex.

In this study we compare the physicochemical properties and the catalytic effectiveness for the oxidation of mercaptan of Mg–Al hydrotalcite compounds including cobalt(II) phthalocyanine tetrasulfonate prepared by DS, AE and SR.

2. Experimental

2.1. Catalysts synthesis

Three methods of synthesis were used. Whatever the method, all the samples were prepared with the same Mg/Al ratio (2.5) and equal content of cobalt(II) phthalocyanine tetrasulfonate.

DS sample. The catalyst was synthesized wherein two solution, one of Mg and Al nitrates, the second of cobalt(II) phthalocyanine tetrasulfonate and NaOH. The solutions were added simultaneously in a necked flask while maintaining the temperature at 333 K with vigorous stirring under helium atmosphere to minimize contamination by atmospheric CO_2. The addition of all the two solutions took nearly 3 h. The precipitate formed was aged in its mother liquor for 18 h at 333 K and then filtered, washed with hot distilled water and dried overnight at 343 K.

AE sample. A hydrotalcite $[Mg_5Al_2(OH)_{12}][TA]\cdot mH_2O$ (TA: terephthalate dianion) was prepared as described earlier by Dredzon [20]. The wet freshly prepared slurry was added to a solution containing the sodium salt of the $CoPcTs^{4-}$ complex. The mixture was then stirred and aged at 333 K for 40 h under helium atmosphere. The obtained material was filtered, washed with hot distilled water and dried overnight at 343 K.

SR sample. A hydrotalcite of the type $[Mg_5Al_2(OH)_{14}][CO_3]\cdot mH_2O$ was prepared by the coprecipitation of Mg^{2+} and Al^{3+} in the presence of carbonates using a method described earlier by Reichle [22]. The Mg–Al hydrotalcite obtained was converted to a metal oxide solid solution by heating at 723 K for 18 h. The solid solution was then reconstituted into an hydrotalcite by interaction with an aqueous solution of the sodium salt of the $CoPcTs^{4-}$ complex at 333 K for 7 days under helium atmosphere. The obtained material was then filtered, washed with hot distilled water and dried overnight at 343 K. The final temperature of drying, always the same for the three samples was selected in order to avoid the decomposition of the cobalt phthalocyanine.

2.2. Characterizations

Elemental analysis of Mg, Al and Co were carried out by inductively coupled plasma using a TJA IRIS-HR spectrometer after dissolving the compounds in a minimum amount of hydrochloric acid. The solid hydration was evaluated by the Karl Fischer method [23]. X-ray diffraction analyses (XRD) were recorded on a Siemens D-500 diffractometer with a graphite-filtered Cu Kα radiation (1.5405 Å). Surface composition was measured by X-ray photoelectron spectroscopy (XPS) with a SSI X-probe (SSSX-1000/206) photoelectron spectrometer. An ASAP 2000 Micrometrics apparatus measured specific surface areas by nitrogen-adsorption after degassing the samples in situ at 353 K for 4 h.

2.3. Reaction procedures

Screenings. The catalytic effectiveness of the DS, AE and SR samples was compared to an industrial catalyst (impregnated active charcoal) using a short time reaction test (36 h). The apparatus consist of a fixed-bed reactor containing 1 g of catalyst. Hydrocarbon feed (carbureactor containing 122 ppm RSH) and air (atmospheric pressure) are passed through the reactor with a space velocity of 1.2 h^{-1} at room temperature. The residual mercaptan content was determined using the silver nitrate potentiometric titration method [24].

Pilot test. The DS catalyst was tested in a long period (17 days) with an apparatus modeling the fixed-bed sweetening process. The apparatus consist of a fixed-bed reactor containing 100 g of 1 mm catalyst particles. Hydrocarbon feed (carbureactor containing 125 ppm RSH) and air (6 bar) are passed through the reactor with a space velocity of 1.2 h^{-1} at 313 K. The residual mercaptan content was also determined using the same silver nitrate potentiometric titration method [24].

3. Results and discussion

3.1. Characterization

Elemental analysis results reported in Table 1 indicate a superior content of Mg and Al in the DS sample. Moreover, this solid retains more cobalt than the other two samples. The low content per unit mass of magnesium, aluminum and cobalt in the SR sample can be explained, as reported in Table 1, by a high hydration level due to the SR method namely: interaction, for 7 days, of the Mg–Al mixed oxide with an aqueous solution containing the $CoPcTs^{4-}$ complex. For the AE solid, very low Mg, Al and cobalt content are explained by the same phenomena (high hydration level) and in addition to the presence of terephthalate. XRD patterns indicated a good crystallization of the three catalysts. AE sample shows a d_{003} reflection of 14.4 Å corresponding to a perpendicular intercalated TA. The organic anion is still intercalated into the intergallery of the hydrotalcite material even with the optimal conditions for AE. For this catalyst we assume a bad retention of the cobalt phthalocyanine due to the occupied interlayer space. For the DS sample we observe a d_{003} reflection at 7.8 Å which correspond to a Mg–Al–CO_3 hydrotalcite. Comparing this result to those obtained by Carrado et al. [19] on copper phthalocyanine tetrasulfonate it is important to notice that the same phenomena was obtained for stoichiometric amount of CuPcTs [19]. Nevertheless for a CuPcTs concentration corresponding to twice that necessary to balance the charge created by aluminum in the hydrotalcite framework, Carrado obtained a perpendicular intercalated Cu phthalocyanine complex with a d_{003} reflection at 23 Å [19]. This component presented however an unexpectedly low surface area of about 0.2 m^2/g as compared with 65 m^2/g for our sample. In the present work we presume a parallel orientation of the cobalt phthalocyanine between the hydrotalcite sheets. This hypothesis was confirmed by a second DS in which we omitted voluntary the addiction of the cobalt(II) phthalocyanine tetrasulfonate. The solid obtained was not a Mg–Al hydrotalcite but $NaNO_3$ (nitratine). This important result indicates that $CoPcTs^{4-}$ contribute certainly to the charge compensation in the DS hydrotalcite sample. A parallel orientation of $CoPcTs^{4-}$ in the observed interlayer spacing is conceivable due to its planar geometry [20]. XRD pattern of the SR sample did not indicate intercalation of the cobalt phthalocyanine since the d_{003} reflection is 7.8 Å. This result different from Pinnavaia and coworkers [21] result could be explained by a lower $CoPcTs^{4-}$ concentration used in this synthesis. XPS results reported in Table 1 show that the DS sample, in contrary to AE and SR, does not present any cobalt at the solid surface even though the ICP indicate that the DS catalyst contains more cobalt than the other two solids. This result supports the presumption of an intercalation of $CoPcTs^{4-}$ in the DS catalyst. Surface area of about 70 m^2/g (N_2/BET) is obtained for the three catalysts but differences are observed in the pore structure (Table 1).

3.2. Catalytic activity

Mercaptans are known [1] to be oxidized into disulfides by air under caustic conditions and in the presence of cobalt(II) phthalocyanine catalyst as follows:

$$2RSH + \tfrac{1}{2}O_2 \rightarrow RSSR + H_2O$$

An anion-radical mechanism was proposed by Wallace et al. in 1964 [25]. The authors suggested the activation

Table 1
Physicochemical properties

Sample	ICP			Karl Fischer hydration (%)	XPS, Co (at.%)	XRD, d_{003} (Å)	BET	
	Mg (mmol/g)	Al (mmol/g)	Co (mmol/g)				SA (m^2/g)	Mean meso pore (Å)
DS	16.86	7.82	0.37	0.9	0	7.8	65	50.5
AE	4.7	3.21	0.086	1.27	0.35	14.4	63	220.5
SR	7.46	3.13	0.097	1.63	0.07	7.8	79	142.2

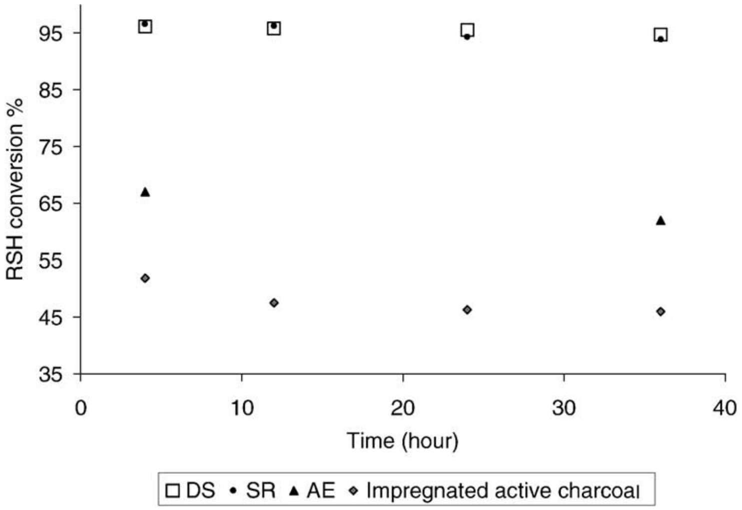

Fig. 1. Mercaptan conversion as a function of time for different catalysts in screening tests.

of mercaptan RSH into RS^- specie by a base, followed by an oxidation of RS^- to $RS^\bullet$ by the cobalt phthalocyanine. The effectiveness of the bifunctional prepared catalysts was evaluated by a simple laboratory experiment with sour distillate containing known amounts of mercaptans. For comparison we realized the same experience with an industrial non-basic impregnated active charcoal. The results, reported in Fig. 1, show a higher catalytic activity of the prepared solids compared to the industrial catalyst, confirming our interest to hydrotalcite materials.

The differences observed between the prepared catalysts could be discussed in terms of basic character and cobalt content (oxidant function). As described by Constantino and Pinnavaia [26,27] for the decomposition of MBOH to acetone and acetylene by $MgAlCO_3$ hydrotalcite at 353 K, the basic character is attributed to $CO_3{}^{2-}$ interlayer anions. The AE sample intercalating the TA and keeping a low amount of cobalt phthalocyanine is the less active. The SR and DS catalyst are acutely active because a meaningful contamination by $CO_3{}^{2-}$ in the case of SR sample

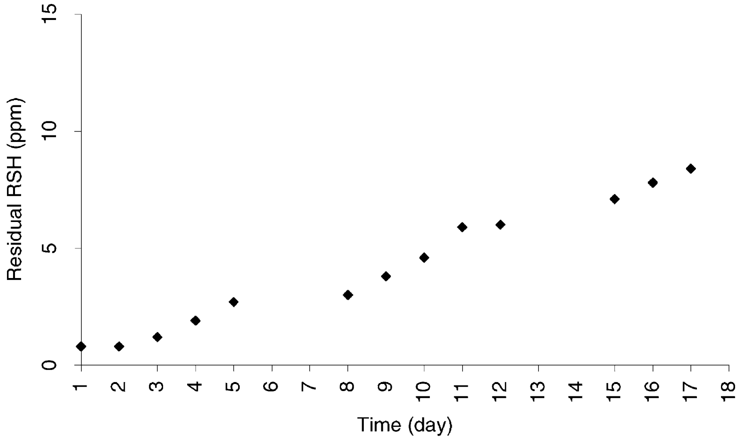

Fig. 2. Residual mercaptans as a function of time for DS catalyst in a pilot test.

and important cobalt content in the case of the DS catalyst.

For the pilot test (reactor containing 100 g of catalyst particles), the SR and AE catalysts fails due to mechanical resistance problems. To solve this dilemma, extrusion of a moisture (catalyst + SiO_2 binding agent) through holes of 1 mm dies followed by a post-treatment at 673 K to consolidate the extrudate was necessary [28]. The Co(II) phthalocyanine contained in SR and AE solids cannot unfortunately resist to this high temperature treatment. For this reason the only catalyst employed in the pilot test modeling the fixed-bed sweetening process was the DS one. On this later solid the cake formed by DS, when dried at 343 K, gives a very resistant material, which was simply broken up and sieved to separate the desired 1 mm particles. The pilot test result, shown in Fig. 2, reports the residual mercaptan as a function of time. Knowing that the actual norm of mercaptan amount in carbureactor product is about 15 ppm maximum, we observed after 1 day, a residual mercaptan of about 0.8 ppm corresponding to 99.4% removal. The amount of RSH increases slowly until 8.4 ppm after 17 days testing. This low deactivation is probably due to the numberless impurities contained in the hydrocarbon feed. Addition of active charcoal by mechanical crossing in the fixed-bed reactor or incorporated it into the final catalyst could probably remove these impurities and improve the lifetime of the catalyst.

4. Conclusion

Without alkali medium a very good mercaptan removal using a bifunctional catalyst was obtained. This catalyst consists of Co(II) phthalocyanine parallel-intercalated Mg–Al hydrotalcite obtained by DS method. Moreover it exhibited a good mechanical resistance which does not need further post-treatment to improve physical properties.

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