PRELIMINARY STUDIES CONCERNING CATALYTIC OXIDATION OF ALKYL MERCAPTANS FROM LIQUID PETROLEUM CUTS IN THE PRESENCE OF FE(III) CHELATES SUPPORTED ON HYDROTALCITE-LIKE COMPOUNDS

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abstract: The aim of this work is to prepare a bifunctional solid catalyst to convert unwanted mercaptans from the petroleum cuts into disulfides, avoiding the consumption of a non-easily regenerated caustic solution. Catalysts containing Fe(III)EDTA-citrate chelate supported on Mg-Al hydrotalcite were prepared by impregnation method. Their activity for mercaptans oxidation was tested and compared to that of the neat support and the one exhibited by the pure iron chelate in alkaline solution. In the presence of the hydrotalcites-supported catalysts, conversions of methyl-mercaptan to disulfide higher than 85% were obtained even if the initial concentration of mercaptan was relatively high.

keywords: Mg–Al hydrotalcite, Mercaptan oxidation, iron chelates

Introduction

Mercaptans present in crude oil and petroleum cuts are toxic and corrosive impurities distributed among petroleum products. Therefore, it is necessary to remove them, either by extraction or by their subsequent transforming to inoffensive alkyl disulfides. In the petroleum industry, such processes are usually called "sweetening". The most widely used process of sweetening is Merox developed by UOP [1-3]. This process is based on the ability of a metal chelate, i.e. sulfonated cobalt phthalocyanine (CoPcS), to catalyze the oxidation of mercaptans to alkyl disulfides under caustic condition by molecular oxygen or by air. The overall reaction of the process is:

$$2\textbf{RSH} + 1/2\textbf{O}_2 \xrightarrow[\textbf{OH}^-]{\text{Merox Catalyst}} \textbf{RSSR} + \textbf{H}_2\textbf{O}$$

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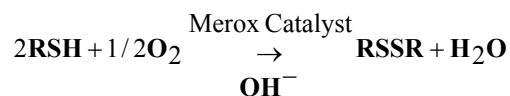
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The reaction consists of two major steps: first, mercaptan is transformed to mercaptide anion by a base (sodium hydroxide or ammonia); second, mercaptide is oxidized to dialkylsulfide via the formation of a ternary complex involving CoPcS, mercaptide anion and molecular oxygen. The ligand, RS^- binds to CoPcS more strongly than RSH, so the first step, in which RSH is converted to RS^- by a base, is of primary importance to sweetening. Besides this process, which is currently utilized in refineries, there are literature data [4-10] claiming the possibility of mercaptans oxidation with oxygen at pH=8,5-10 and ambiental temperature and pressure in the presence of transitional metal (Fe, Co, Cr, or V) chelates solutions. The global process, which is similar to Merox, consists in aerobic oxidation of alkyl-mercaptans to alkyl-disulfides using as catalysts chelates of transitional metals in their high oxidation state. The reducing of the transitional metal ion by RS^- takes place simultaneously with the oxidation of the reduced species by the oxygen.

A fundamental problem of the above mentioned procedures is associated with the use of caustic solutions which cannot be converted to a valuable product. Even worse, their discharge enhances the costs of the environmental protection. Overcoming this situation requires minimizing or eliminating the use of caustic solutions wherever possible. Solid bases emerge as an ideal alternative to the aqueous bases to overcome this problem. Aqueous alkali can be completely replaced in the mercaptan oxidation reaction by incorporating solid basic materials into the catalyst formulation [1,11]. In a previous work it has been shown that Fe (III) EDTA-citrate chelates which are stable at high values of pH are promising catalysts for alkyl-mercaptans oxidation [5].

Therefore, in this paper we considered it would be interesting to investigate the oxidation of alkyl-mercaptans to alkyl-disulfides in the presence of Fe(III)EDTA-citrate chelate supported on a hydrotalcite-like compound (HTlc) playing the role of a solid base.

Experimental

The catalyst preparation utilised the following reagents without a previous purification: $Mg(NO_3)_2 \cdot 6H_2O$ (p.a) REACTIVUL min. 99.5 %; $Al(NO_3)_3 \cdot 9H_2O$ p.a. RIEDEL-DE HAËN AG min. 98.5 %; NaOH p. a. CHEMAPOL min. 98 %; Na_2CO_3 – p.a. CHIMOPAR min. 99.8 %, $Fe(NO_3)_3 \cdot 9H_2O$ p.a. (MERCK) min. 99%; $Na_2EDTA \cdot 2H_2O$ p.a. (MERCK) min. 99.2% ; citric acid anh. (REACTIVUL) min. 98%.

The preparation of the iron chelate Fe(III)EDTA-citrate (K) was performed according to the method previously described [5, 12].

The hydrotalcite support (HT) with the general formula $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ (Al/(Al+Mg)=0.25) was prepared by co-precipitation at pH 10 and low super saturation according to the method described by A. Corma and R. M. Martin-Aranda [13,14]. Two solutions A and B were contacted at 25ºC by feeding with a flow rate of 60 mL·h^{-1} and were mixed under vigorous and continuous stirring. Solution A was prepared by solving $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in distilled water yielding a 1.5 M final concentration of Al+Mg. Solution B was prepared by solving NaOH and Na_2CO_3 enabling that the

mixture of A+B fulfills the following requirements: $CO_3^{2-}/(Al+Mg)=0.666$ and $OH^-/(Al+Mg)=2.25$.

The pH of the precipitates was maintained at 10, either by adjusting the flow rate of the alkaline solutions or by using 1 M NaOH or 1 M HNO_3 solutions. After addition of the reactants, the slurry was aged at 65^0C for 18 h in a thermostatic bath under mild stirring. A reflux unit was mounted on top of the vessel to prevent water evaporation. The resulting product was cooled at room temperature, filtered, washed thoroughly with a large amount of warm deionized water until neutral pH of the washing water was reached and subsequently dried at 90^0C for 18 h.

The catalyst consisting of Fe(III)EDTA chelate supported on HT was prepared by impregnation according to the method described in literature [15, 16]. The catalyst is further referred to as $K_{1.9}/HT$, where the index represents the iron concentration as determined by chemical analysis.

The solids were characterized by chemical analysis, XRD, and FTIR spectroscopy. X-ray diffraction analysis (XRD) was performed on a DRON-DART UM 2 diffractometer equipped with a monochromator graphite crystal ($\lambda_{CuK\alpha}$=1.5418 Å). The samples were scanned from 8° to 70° (2θ) in steps of 0.05^o with an acquisition time of 2 s at each point. The profile fitting calculations were performed using Jandel Scientific computer software and Voigt functions. FTIR spectra in the range 400-4000 cm^{-1} were recorded on a Perkin Elmer 1600 FTIR spectrometer using the KBr pellets technique.

The catalytic tests for alkyl-mercaptans (RSH) conversion were performed at ambiental temperature and pressure, under continuous stirring using as catalysts the solution of iron chelate (K), the parent hydrotalcite (HT), and the hydrotalcite-supported iron chelate $K_{1.9}/HT$. Synthetic samples of gasoline (100 ml) containing 200 ppm and 325 ppm alkyl-mercaptans (methyl- and *tert*-buthyl mercaptan) were submitted to oxidation under air flow (0.5L/h) in the presence of the above mentioned catalysts. Catalytic tests were carried out during 60 minutes, and the residual content of RSH was determined at 10 minutes intervals by titration with 0.01 N $AgNO_3$ alcoholic solution in the presence of dithizone according to the method described in a previous work [17].

Results and Discussion

XRD patterns presented in Fig. 1 show that the parent HT crystallizes in a hexagonal framework with rombohedral symmetry belonging to space group *R3m*. The parameters of the elementary cell were calculated according to the formulas: a= 2x d_{110}, and c=1.5 x (d_{003}+ 2d_{006}). The structural data are presented in Table 1. The interlayer distance has been calculated using Miyata's evaluation of the brucite-type layer thickness 4.8 Å [18]. Since the XRD patterns of $K_{1.9}/HT$ and $K_{3.5}/HT$ were identical, in Fig. 1, only the spectrum of $K_{1.9}/HT$ is presented. The XRD patterns show that both the parent HT and $K_{1.9}/HT$ have a well crystallized hydrotalcite structure. The pattern of the sample containing the iron chelate does not present significant modifications compared to HT since the values of the structural parameters are very similar in the limits of experimental errors. The slight decrease of the

basal spacing reflections illustrated by the lower ratios I_{003}/I_{110}, may be a consequence of a new arrangement of the species in the interlayer space. The presence of diffraction lines corresponding to iron salt-like impurities has not been detected in the XRD pattern of $K_{1.9}/HT$. A slightly higher background of $K_{1.9}/HT$ diffraction pattern could be a consequence of the high dispersion of the iron species, more likely on the outer surface of the hydrotalcite crystals than in the interlayer region.
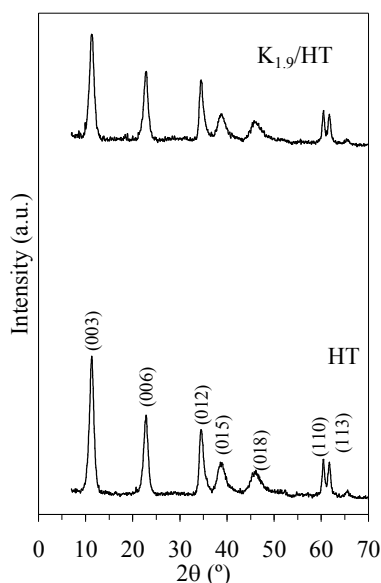

Fig.1. *XRD pattern of HT and $K_{1.9}/HT$*

Table 1. Structural data calculated from XRD analyses of HT and $K_{1.9}/HT$

Sample	*a* (Å)	*c* (Å)	I_{003}/I_{110}	Interlayer distance (Å)
HT	3.06	23.46	3.84	3.02
$K_{1.9}/HT$	3.06	23.44	3.47	3.01

The FTIR spectra of the catalyst samples, in the range of 400-4000 cm^{-1}, are shown in Fig. 2. The spectrum of HT used as support presents the characteristic adsorption bands for $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ at 410, 629, 841, 1386, 1521, 1660 and 3562 cm^{-1} [14,15, 19]. In the spectrum of the pure iron chelate (K) the most intense adsorption bands appear at: 550 cm^{-1}; 830 cm^{-1}; 1060 cm^{-1}; 1320 cm^{-1}; 1580 cm^{-1}; 2280 cm^{-1}; 3300 cm^{-1} [5]. In the spectrum of the hydrotalcite-supported iron chelate the adsorption maximums are noticed at 610 cm^{-1}; 1050 cm^{-1}; 1340-1350 cm^{-1}; 1560 cm^{-1}, and 3400 cm^{-1}. The band corresponding to the vibration of the structural OH groups hydrogen bonded with interlamellar water molecules in HT are shifted from 3562 cm^{-1} towards 3400 cm^{-1}. Also the appearance of a shoulder of this band around 3300 cm^{-1} may be related to the presence of the complex. The bands in the region 600-1600 cm^{-1} are much broader than those observed in the spectrum of the pure hydrotalcite and they are also shifted to lower wavenumbers. This fact may be a consequence of the overlapping of the bands of the neat complex with those characteristics for HT.
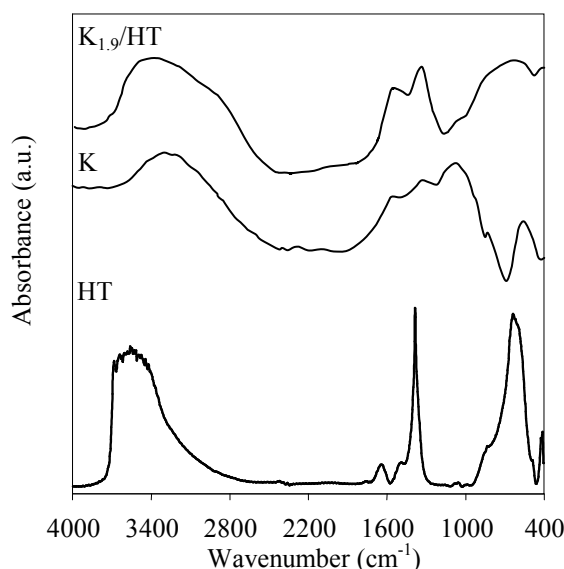
Fig. 2. *FTIR spectra of catalysts samples*

A first set of reactions concerned the catalytic activity for the oxidation of RSH to corresponding alkyl-disulfides. Samples of gasoline containing 325 ppm of RSH (MeSH, *t*-BuSH) were submitted to oxidation under air flow (0.5L/h) in the presence of different amounts of supported iron chelate catalyst, in order to find out the optimum value of the gravimetric ratio Fe/RSH necessary for reaching the highest conversion of RSH. The results obtained for $K_{1.9}$/HT were compared to those obtained in the tests performed in homogeneous system using an amount of iron chelate solution containing the same quantity of iron as in supported catalyst. The catalytic activity of the parent HT was also investigated under the same reaction conditions, using a mass of solid equal to the one utilised in the tests with $K_{1.9}$/HT. The conversion of RSH on HT did not exceed 14.2 in the case of MeSH and 10% in the case of *t*-BuSH, respectively, regardless the amount of solid used as catalyst. It may be assumed that on HT, the reaction takes place probably due to the basic sites of the solid, which play the role of enhancing the dissociation of RSH favouring their subsequent oxidation.

The results presented in fig. 4, show that the conversion of RSH to RSSR is slightly higher for the supported iron chelate catalyst than for the unsupported one. This fact may be a consequence of a better dispersion of the active iron chelate species on the surface of the supported catalyst. Therefore, the main advantage of using the hydrotalcite-supported iron chelate catalyst is related more to avoiding the use of the alkaline solution. The results show that at the same reaction time, and initial concentration of mercaptans the conversion to disulfides is different depending on the nature of the mercaptan. The conversion of MeSH is always higher than the conversion of t-BuSH. The lower reactivity of *t*-BuSH may be a consequence of its bigger molecular-size, which imposes diffusion constrains [3].
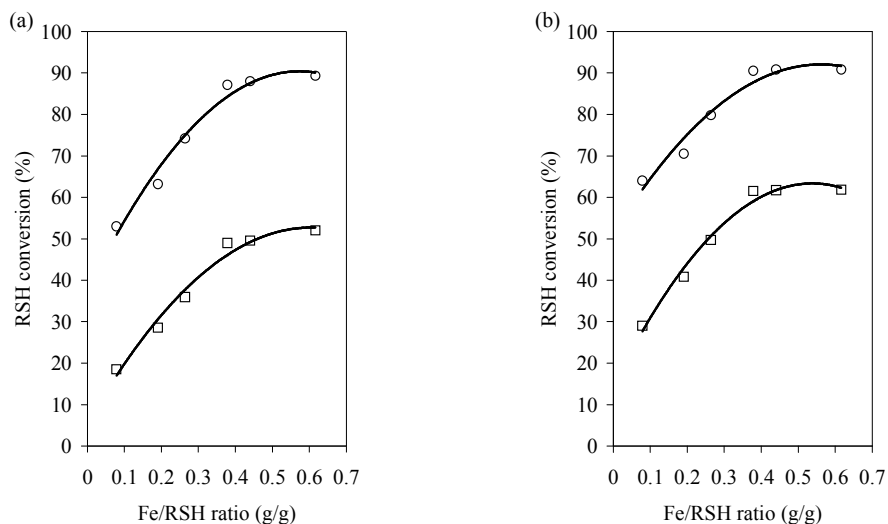
Fig. 4. *Dependence of RSH oxidation on the ratio Fe/RSH for (a) K, and (b) $K_{1.9}$/HT ; ○ – MeSH, □ -t-BuSH. Initial concentration of RSH = 325 ppm, Reaction time 30 minutes, Air flow (0.5 L/h)*
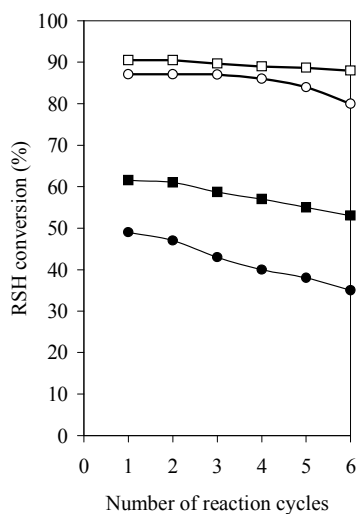

Fig. 5. *Conversion of mercaptans to disulfides as a function of the number of reaction cycles: ■ – conversion of t-BuSH on K1.9/HT ● – conversion of t-BuSH on K, □-conversion of MeSH on K1.9/HT, ○-conversion of MeSH on K. Initial concentration of RSH 325 ppm, gravimetric ratio Fe/RSH=0.4 g/g Air flow (0.5 L/h)*

The second set of experiments aimed to investigate the resistance of the catalyst under operating conditions and the possibility of using it in repeated reaction cycles. The duration of 1 cycle was 30 minutes. The catalyst used in one reaction cycle was separated from the reaction mixture and dried in the oven during 1 hour at 45°C. Afterwards it was introduced in the next reaction cycle. Since the previous tests showed that the increase of the

gravimetric ratio Fe/RSH above 0.4 g/g does not lead to significant enhancing of RSH conversion, these tests were performed using an amount of $K_{1.9}$/HT catalyst corresponding to this ratio. The results are presented in fig.5.

From fig. 5 it may be seen that the loss of the catalytic activity is lower in the case of MeSH conversion than in the case of *t*-BuSH. The more pregnant decrease of the activity for *t*-BuSH oxidation could be a consequence of the lower solubility of *tert*-buthyl-disulfide in the organic phase compared to that of the dimethyl disulfide. This fact could induce higher mass transfer limitations either at the liquid-liquid interface when using K catalyst or to a saturation effect due to the accumulation of disulfides on the surface of the solid catalyst $K_{1.9}$/HT and a subsequent screening of the active sites.

Conclusion

The above presented results shown that hydrotalcite-supported iron chelate Fe(III)EDTA-citrate are active catalysts for the conversion of mercaptans to disulfides. They present also a better stability during repeated reaction cycles compared to the stability of the complex used in liquid phase conditions. This fact may be related to the dispersion of the active phase at molecular level on the surface of the carrier, allowing a better contact between the reactants and the active sites. Due to its base properties, the hydrotalcite support favours also the dissociation of mercaptans, playing a role similar to the one of the alkaline solutions used in homogeneous conditions. It presents also the advantage that it can be easier separated from the reaction mixture and does not imply any corrosion effects.

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