Catalytic Oxidative Demercaptanization on Mg-Al Hydrotalcites Containing Cobalt Complex Anions

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The catalytic activity of trihydrocarbylphosphinetrihalocobaltate complexes $[R_3PCoX_{3-n}X'_n]^-$, R=C_6H_5 or n-C_4H_9 and X=Cl; X'=Br, n=0 or 1 immobilised in hydrotalcite $Mg_{0.75}Al_{0.25}$ (HT) utilised for the oxidative demercaptanization of toluene contaminated by different alkane-thiols (ethanethiol, isopropylthiol, tert-butyl-thiol) and thiophenol is investigated and compared to that of tetrasulphonated Co-phtalocyanine /HT. The performances of the catalysts depend on the nature of the ligands bonded on the Co atom as well as on the oxidation susceptibility of the substrate. The variation of the activity as a function of time was investigated by performing successive cycles of oxidative demercaptanization reaction-catalyst regeneration.

Keywords: cobalt complex anions, tetrasulphonated Co-phtalocyanine, cobalt phosphine complex, oxidative demercaptanization

Heterogeneizations of transition metal complexes by encapsulation in zeolite supercages [1-3], or by anchoring them in pillared clays such as hydrotalcites (HTs) [4-9] are currently under study as modalities for obtaining more active catalysts than their homologues in solution.

In HTs with general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$ the cations M^{2+} and M^{3+} are occupying the central positions in $M(OH)_6$ octahedrons, which are edge-connected forming the sheets with positive charges while the A^{n-} and H_2O are the interlayer anions and water molecules. In order to maintain the electrical neutrality of the lattice, the positive charges are balanced by A^{n-} [9].

The brucite-like sheets of HTs are the host species and the interlayer anions and water molecules are the guest species**.** The HTs are nominated as supramolecular layered double-hydroxides because the host and guest species are combined into two-dimensional supramolecular layered solid via electrostatic and hydrogen bonding interactions. In these solids, ion-exchange reaction can occur between the interlayer guest species and other molecules or anions with suitable size and shape, which can enter into the gallery. The interlayer spacing depends on the dimension and geometry of the new guest [10] as it has been proved when synthetic porphyrines, phtalocyanines, Schiff-base complexes [4-9], and bis(2-mercapto-2,2'diphenyl-ethanoate]dioxo-molybdate(VI) complex [11, 12] have been immobilised into HTs. These types of catalysts have been used in oxidations of mercaptans [4-6], inorganic cyanides [7] and phenols [4,5].

The catalytic activity of metal complexes immobilised into HTs, especially Co(II)phtalocyanine-tetrasulfonate $[Co(PcTS]^{4-}$, which has oxygen carrier properties have been studied for the oxidation of thiols with O_2 at 298-313K [13]. This "sweetening process", which is more advantageous from an economical point of view when compared to hydroprocessing [14], is a technology for treating FCC gasoline and other petroleum cuts in order to remove the mercaptans according to the reaction:

$$4\,RSH + O_2 \rightarrow 2\,RSSR + 2\,H_2O \qquad (1)$$

In aqueous conditions addition of a base is necessary (*p*H=9-9.5) because in the initial step a mercaptide ion has to be formed [15]. The immobilisation of the transition metal complex into HTs has three main effects on the catalytic behaviour. First, the activity of Co complex is improved by heterogeneization; second, the catalyst is more stable in time than the homogeneous homologue, and third, the HTs or the mixed oxides obtained from HTs precursors not only acts as a carrier but also as a solid base [8].

Based on the above mentioned premises we have assumed that besides $[Co(PcTS]^{4-}$, other Co-complex anions such as trihydrocarbylphosphinetrihalocobaltate $[R_3PCoHal_3]^-$, where R=hydrocarbyl radical, and Hal=halide ion immobilised on HTs could be active catalysts for the sweetening processes.

To our knowledge, the aspects concerning the preparation of HTs containing $[R_3PCoHal_3]^-$ anions and their activity for the sweetening process involving the oxidation of thiols to alkyl disulfides has not yet been reported. Therefore, in the present work we report the results concerning the preparation, the characterization and the catalytic activity of several new catalysts obtained by the incorporation of different Co-complex anions $[R_3PCoX_{3-n}X'_n]^-$, where R=C_6H_5; *n*-C_4H_9 and X=Cl; X'=Br, n=0 or 1 in the interlamellar space of $Mg_{0.75}Al_{0.25}$ hydrotalcite-type structure.

The effects induced by the different types of ligands on the performances of these catalysts in the oxidation of ethanethiol to diethyl disulfides have been investigated. For the most active type of complex catalyst, the influence of the transitional metal content in HTs supported samples on its activity has been determined. Tests for the oxidation of several thiols characterised by different oxidation susceptibility have been performed using the most active catalyst.

The results of all catalytic tests were compared to those obtained with standard catalysts consisting in cobalt-phtalocyaninetetrasulphonate $[CoPcTS]^{4-}$ immobilised in HTs containing the same concentration of Co.

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Table 1

CHEMICAL COMPOSITION OF THE HYDROTALCITE - SUPPORTED COMPLEXES, Mg:Al ATOMIC RATIO = 3:1

[complex anion]/HT_{xCo}[a]	Co (wt. %)	Atomic ratios determined by chemical analysis (det) / *Atomic ratios calculated from the formula (calc)*				
		$Co:S_{det.}$ / *$Co:S_{calc.}$*	$Co:N_{det}$ / *$Co:N_{calc.}$*	$Co:P_{det.}$ / *$Co:P_{calc.}$*	$Co:Cl_{det.}$ / *$Co:Cl_{calc.}$*	$Co:Br_{det.}$ / *$Co:Br_{calc.}$*
$[CoPcTS]^{4-}/HT_{2.3Co}$	1.3	1:3.9 / *1:4*	1:8.1 / *1:8*	-	-	-
$[CoPcTS]^{4-}/HT_{4.5Co}$	2.6	1:3.96 / *1:4*	1:8.12 / *1:8*	-	-	-
$[CoPcTS]^{4-}/HT_{9Co}$	5	1:3.98 / *1:4*	1:8.15 / *1:8*	-	-	-
$[CoPcTS]^{4-}/HT_{13.5Co}$	7.8	1:4 / *1:4*	1:8.18 / *1:8*	-	-	-
$[CoPcTS]^{4-}/HT_{20Co}$	11.6	1:4.02 / *1:4*	1:8.22 / *1:8*	-	-	-
$[CoCl_3P(C_6H_5)_3]^-/HT_{2.3Co}$	1.3	-	-	1:1.17 / *1:1*	1:2.92 / *1:3*	-
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	2.6	-	-	1:1.22 / *1:1*	1:3 / *1:3*	-
$[CoCl_3P(C_6H_5)_3]^-/HT_{9Co}$	5	-	-	1:1.25 / *1:1*	1:2.98 / *1:3*	-
$[CoCl_3P(C_6H_5)_3]^-/HT_{13.5Co}$	7.8	-	-	1:1.28 / *1:1*	1:3.02 / *1:3*	-
$[CoCl_3P(C_6H_5)_3]^-/HT_{20Co}$	11.6	-	-	1:1.33 / *1:1*	1:3.05 / *1:3*	-
$[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$	2.6	-	-	1:1.24 / *1:1*	1:1.97 / *1:2*	1:1.1 / *1:1*
$[CoCl_3P(n\text{-}C_4H_9)_3]^-/HT_{4.5Co}$	2.6	-	-	1:1.23 / *1:1*	1:1.97 / *1:2*	-
$[CoCl_2BrP(n\text{-}C_4H_9)_3]^-/HT_{4.5Co}$	2.6	-	-	1:1.2 / *1:1*	1:1.94 / *1:2*	1:1.15 / *1:1*

[a] x = Co concentration in micromoles/gram

Experimental part

Catalyst Preparation

The support $Mg_{0.75}Al_{0.25}$ hydrotalcite, (HT), was synthesized using the procedure described in detail earlier [16,17].

The benzyltrihydrocarbylphosphonium trihydrocarbylphosphinetrihalocobaltate complexes used in the preparation of the catalysts are quaternary salts having the formula: $[C_6H_5\text{-}CH_2\text{-}PR_3]^+[R_3PCoX_{3-n}X'_n]^-$ where R=C_6H_5 or *n*-C_4H_9, X=Cl and X'=Br, *n*=0 or 1. The structure and preparation of the related Ni compounds has been earlier described by Cotton et al. [18]. A similar preparation procedure was developed by Eberhardt et al [19] for the obtaining of the Co complexes according to the reaction:

$$2R_3P + CoCl_2 + C_6H_5\text{-}CH_2\text{-}Hal \rightarrow [C_6H_5\text{-}CH_2\text{-}PR_3]^+[CoCl_2HalPR_3]^- \quad (2)$$

which takes place while heating under N_2 at 70°C for 6 h a mixture of trihydrocarbylphosphine (0.02 mole), $CoCl_2 \cdot 6H_2O$ (0.01 mole) and benzylhalide (0.01 mole) in *n*-butanol.

The precipitate is separated by filtration under nitrogen. The following complexes have been prepared:

$[C_6H_5\text{-}CH_2\text{-}P(n\text{-}C_4H_9)_3]^+[CoCl_3P(n\text{-}C_4H_9)_3]^-$,$[C_6H_5\text{-}CH_2\text{-}P(n\text{-}C_4H_9)_3]^+[CoCl_2BrP(n\text{-}C_4H_9)_3]^-$, $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$ and $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$.

The preparation of the intercalated complex anions into the galleries of the hydrotalcite by ion exchange was performed under nitrogen, by stirring during 2 days a solution of complex in acetone and the HT sample. The reaction product was washed with acetone and dried at room temperature under nitrogen.

The standard catalysts based on $[CoPcTS]^{4-}$ immobilised in HT, were obtained according to the method described by Pinnavaia et al. [4,5] using the appropriate amounts of $Na_4[CoPcTS]^{4-}$ aqueous solution. $Na_4[CoPcTS]^{4-}$ was purchased from Merck.

Catalysts Characterisation

The chemical compositions of the neat complexes as well as of the catalysts have been determined by elemental analysis (for the determination of C, H, N amounts in complexes), chemical analysis for determination of Cl, Br, P, Mg, Al, atomic absorption spectrometry for the determination of Co. The analyses of the neat complexes showed that their composition was in good agreement with their chemical formula. The results obtained at the analyses of the hydrotalcite-supported complexes are presented in Table 1.

The catalysts have been also characterized by diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis), FTIR spectroscopy and XRD.

DR-UV-Vis spectra in the range 215-915 nm have been recorded using SPECORD 80 UV-VIS spectrometer with an integration sphere coated with MgO taken as reference. FT-IR spectra in the domain 400-4000 cm^{-1} were recorded on a BioRad FTS 135 spectrometer using the KBr pellet technique.

X-ray diffraction measurements were recorded with a DRON DART UM 2 diffractometer ($Cu\text{-}K_\alpha$ radiation provided by graphite monochromator, $\lambda = 1.5418$ Å) in 2θ range of 6-70° in a step scanned mode (step width 0.05, acquisition time 2 s).

Catalytic tests

The activity of the catalysts was tested in the demercaptanization of a synthetic mixture of toluene and alkanethiol. The demercaptanization reactions were carried out in a 250 mL flask equipped with a condenser, a thermometer and a bubbling device for the admission and bubbling of air. In an experiment 0.35 g of catalyst were added to 100 g of toluene containing different amounts of thiols.

The mixture was magnetically stirred at 25°C and atmospheric pressure, bubbling air continuously with a flow rate of $5L \cdot h^{-1}$.

Liquid samples were collected periodically for the chromatographic dosage of remaining mercaptans.

The catalytic activity was expressed as conversion of mercaptans (%) and TOF (e.g. mmoles of RSH transformed . $(mmoles\ Co)^{-1}$. $(min)^{-1}$).

Results and discussions

Catalysts characterisation

All the DR-UV-Vis spectra presented the characteristic features for pseudo-tetrahedral symmetry of Co(II) [20, 21]. In the UV region the bands corresponding to ligand to metal charge transitions (LMCT) are overlapped by the band corresponding to the tetrahydrocarbylphosphonium cation around 300nm (e.g. 310nm for $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+$ and 300nm for $[C_6H_5\text{-}CH_2\text{-}P(n\text{-}C_4H_9)_3]^+$) [22]. Due to this overlapping all the bands could be seen only by the deconvolution of the spectrum. In the region 900-400nm, the absorption bands characteristic for d-d transitions appear along with the bands corresponding to π-π^*, n-π^* and MLCT (metal to ligand charge transitions) transitions in trihydrocarbylphosphine ligand (e.g. 430nm (π-π^*), and 545 nm (MLCT) for $P(C_6H_5)_3$ or 414 nm and 540 for $P(n\text{-}C_4H_9)_3$) [23, 24].

For clarity (fig. 1) presents only the spectra of the triphenylphosphinetrihalocobaltate complexes immobilised in HT compared to those of the neat benzyltriphenylphosphonium triphenylphosphinetrihalocobaltate complexes. In the region specific for LMCT transitions following the deconvolution of the spectrum of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$ (fig. 1A) the characteristic bands for trichlorocobaltate at 358, 264 and 222 nm [25], along with the band at 310nm characteristic for $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+$ have been evidenced. In the same region, the deconvolution of the spectrum of the $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$ showed that the bands corresponding to trichlorocobaltate have been shifted towards higher wavelengths e.g. 362, 274 and 231 respectively, while the band corresponding to the cation at 310nm diminished drastically its intensity. The shift of the bands indicates the distortion of the complex under the influence of the crystal field of the hydrotalcite support, probably following the interaction with OH groups from the support, as it is also suggested by IR spectra. Taking into account that the preparation of the immobilised complex involved the anionic exchange, it should be expected that the band corresponding to the cation disappears. Since this band is still present in the spectrum of the hydrotalcite-supported samples even if its intensity is very low, it may be assumed that traces of un-exchanged complex remain on the solid. This fact is in agreement with the results concerning the composition of the catalysts presented in Table1, which showed that the P content exceeds slightly the Co content in $[CoHal_3P(C_6H_5)_3]^-$/HT catalysts.

In the spectrum of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$ (fig. 1B-b_1) the bands in the domain 400-215nm are wider than those in the spectrum of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$, and shifted to higher wavelengths, e.g. 366, 270, 229 nm. Also, the band corresponding to the cation is shifted to 317nm. These facts may suggest an increase in the covalent character of the bonds, probably due to the lower electronegativity of Br compared to Cl [20]. In the spectrum of $[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$ five bands could be isolated by deconvolution at 366, 317, 279, 242, and 219 nm. The presence of the last band indicates a strong interaction between the complex and the solid support.

In the visible region, the DR-UV-Vis spectrum of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$ presents two characteristic bands for Co(II) with distorted tetrahedral symmetry at 609 with a shoulder at 654 nm attributed to the $^1A_{1g}$-$^1B_{1g}$ transition [26]. The presence of a supplementary band at 709nm, suggests the presence of a dimeric form of the complex similar to that encountered in the case of phtalocyanines [21, 27]. In the spectrum of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$ this band is shifted to 754nm. The band corresponding to PPh_3 ligand in the anion is shifted to higher wavelengths, e.g. from 439nm to 450nm, while the one at 545nm disappears. A similar trend is observed for one of the bands characteristic to Co(II) with distorted tetrahedral symmetry, which is shifted from 609 to 618nm. These facts suggest a decrease in the ligand field strength in the case of $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$ [20] indicating a more distorted structure compared to the trichloro-complex.

In the spectra of both Co-complex anions immobilised in HT, under the influence of the strong interactions with the crystal field of the hydrotalcite support, the bands at wavelengths higher than 700nm disappear while the band corresponding to (π–π^* transition) in PPh_3 ligand is shifted to higher wavelengths e.g. 450 nm for $[CoCl_3P(C_6H_5)_3]^-$ and 462 nm for $[CoCl_2BrP(C_6H_5)_3]^-$. The main difference

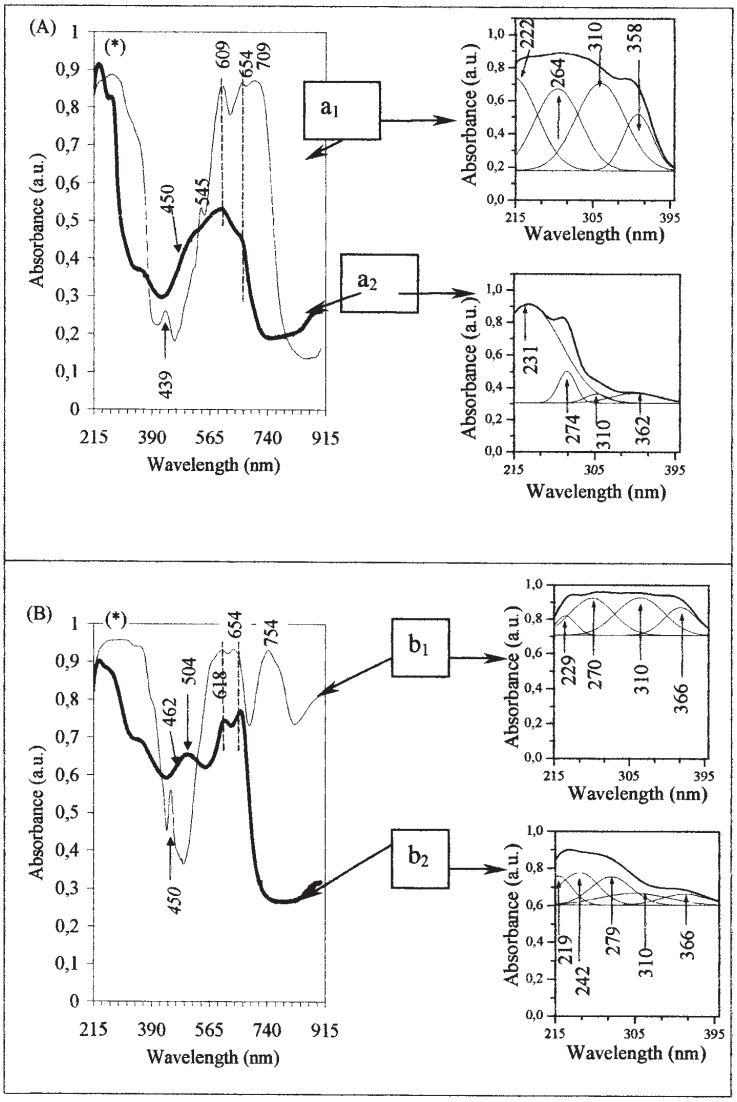


Fig. 1. DR-UV-Vis spectra of the neat cobalt complexes and the cobalt complexes immobilised into $Mg_{0.75}Al_{0.25}$ hydrotalcite, HT: (A) (a_1) $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$; (a_2) $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$; (B) ($b_1$) $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$; ($b_2$) $[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$ (*) wide band in the region 215-400nm, deconvolutions in details

between the electronic spectra of the two samples concerns the bands corresponding to MLCT transitions. Thus, in the spectrum of $[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$ a supplementary broad band at 504nm appears besides the two bands corresponding to distorted tetrahedral symmetry of Co(II) at 618 and 654 nm. This new band indicates the presence of some Co species in octahedral configuration [26]. Meanwhile, in the spectrum of $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$ only the bands characteristic to distorted tetrahedral symmetry Co(II) species at 609 and 654nm are present even if their intensity is rather altered due to the interactions with the crystalline lattice of the support.

The results of FTIR analyses are presented in figure 2.

The spectrum of the parent HT presents the main absorption bands at 3500, 1600, 1358, 1390, 850-880, and 670-690 cm^{-1} corresponding to a typical hydrotalcite structure [9,28]. There are slight differences between the infrared spectra of the two neat complexes, since the vibrations of Co-Cl and Co-Br bonds appear below 400cm^{-1} [29]. In the spectra of the supported complex catalysts the main bands characteristic to phosphine ligand at 3000, 742, 717 and 692 cm^{-1} [30] are covered by the intense bands of the support. However, significant differences appear between the infrared spectrum of $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$ and the spectrum of $[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$. Thus, the spectrum of $[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$ presents broader absorption bands than the spectrum of $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$ suggesting a higher disorder in the interlayer space, probably due to the

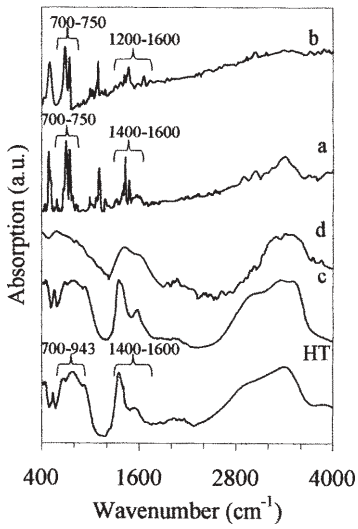


Fig.2. FTIR spectra of the neat cobalt complexes and the cobalt complexes immobilised into $Mg_{0.75}Al_{0.25}$ hydrotalcite (HT),: a-$[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_3P(C_6H_5)_3]^-$; (b) $[C_6H_5\text{-}CH_2\text{-}P(C_6H_5)_3]^+[CoCl_2BrP(C_6H_5)_3]^-$; c- $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$; d-$[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$

stronger distortion of $[CoCl_2BrP(C_6H_5)_3]^-$ complex anion that was indicated also by the results of DR-UV-Vis analysis.

The inspection of the XRD patterns of the anion exchange samples displayed for all of them the typical X-ray powder diffraction patterns of a 3R polytype HT structure (JCPDS file no. 70-2151) without any significant impurity phase. For the samples containing immobilized Co-complex anions, the *a* and *c* cell parameters values

Table 2
STRUCTURAL DATA OF THE PARENT HT AND $[CoCl_3P(C_6H_5)_3]^-$ / HT CATALYSTS WITH DIFFERENT Co CONCENTRATIONS AS INDICATED IN TABLE 1

Sample	Lattice parameters		I_{003}/I_{110}	I_{006}/I_{003}	FWHM (003)
	a (Å)	*c* (Å)			(°)
HT	3.061	23.433	3.79	0.53	1.03
$[CoCl_3P(C_6H_5)_3]^-/HT_{2.3Co}$	3.063	23.493	3.44	0.56	1.04
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	3.064	23.524	3.02	0.63	1.14
$[CoCl_3P(C_6H_5)_3]^-/HT_{9Co}$	3.067	23.877	3.12	0.77	1.17
$[CoCl_3P(C_6H_5)_3]^-/HT_{20Co}$	3.065	23.556	1.28	1.08	1.22

prove a slight modification while the intensities of the basal peaks are considerable lower with a tendency of a gradually increment in the relative intensity of the (006) reflection along with a decrease of the relative intensity of the (003) reflection as the Co-concentration increases. We exemplified this general trend with the XRD spectra of $[CoCl_3P(C_6H_5)_3]^-$/HT samples (fig. 3 and table 2). The broadening of the basal peaks (FWHM values in table) indicates an enhancement of the disorder in the stacking of brucite-type layers as the extent of ionic exchange with Co-complex increases. These features, particularly the inversion of intensity of the two peaks were observed for hydrotalcites containing heavy interlayer molecular species [21, 31] and have been related to the increase in electron density in (001) planes. These results exhibited by all the samples indicate that: i) Co-complex anions replace partially the carbonate anions and their intercalation occurs in a flattened position between layers ii) the anion exchange rate is proportional to the initial Co-concentration attesting that for the selected Co-concentration domain, 2.3-20 micromoles Co/g, the anion exchange rate is relatively high. It is worth to notice that the Al concentration is relatively low (Mg/Al=3) and consequently the anion exchange degree is also rather low, while the "flat" orientation of the anions is geometrically privileged.

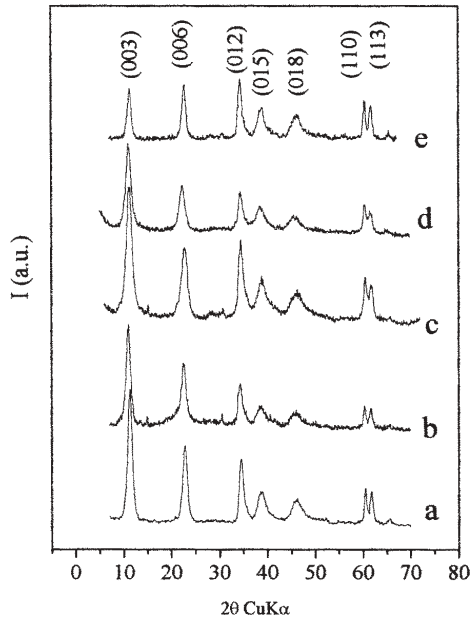


Fig. 3 XRD diffraction patterns for $[CoCl_3P(C_6H_5)_3]^-$/HT catalysts with different concentration of Co compared to the XRD pattern of the parent HT. a- HT; b-$[CoCl_3P(C_6H_5)_3]^-/HT_{2.3Co}$; c-$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$; d-$[CoCl_3P(C_6H_5)_3]^-/HT_{9Co}$; e-$[CoCl_3P(C_6H_5)_3]^-/HT_{20Co}$

Catalytic activity testing

The activity of the complex catalysts prepared and immobilised in HTs containing different amounts of complex anion but the same concentration of transitional metal per gram of catalyst (e.g. 4.5 micromoles Co/gram) has been tested. The results obtained in the oxidation of ethanethiol are presented in table 3.

The catalyst containing $[CoCl_3P(C_6H_5)_3]^-$ as active phase had a demercaptanization activity similar to the one containing cobalt-phtalocyanin-tetrasulphonate anion.

The replacement in the first complex of a chlorine atom with a bromine atom diminishes the catalytic activity less than if the triphenylphosphine ligand is replaced by tri-*n*-butyl-phosphine.

The different delocalisation of the free electronic doublet of the phosphorous atom linked to three radicals with different inductive electronic effects will be reflected in the strength of the coordinative bond Cobalt-Phosphorous and in the electro-accepting capacity of the transitional metal. The access of the reactants to the metal site may be also affected by eventual steric hindrances due to the ligands.

Recently it has been suggested that the general mechanism for the demercaptanization reaction on [CoPcTS] includes the formation of a [CoPcTS]-thiolate complex, which then reacts with oxygen forming an unstable ternary thiolate - [CoPcTS]-O_2 intermediate that should be decomposed rapidly to yield the alkyl-disulphide products according to scheme 1.

The base sites of the hydrotalcite favour the dissociation of the thiols yielding anions RS^- and protons, which are subsequently chemisorbed on the base sites:

$$RSH \leftrightarrow RS^- + H^+ \qquad (3)$$

The anion RS^- reduces the bivalent cobalt cation from the complex [32, 33]

The molecular oxygen coordinated on the reduced Co site oxidises the metal atom generating a dianion $[O_2]^{2-}$ that can easily accept protons yielding H_2O_2 making free the base sites of the support for a new catalytic act [3, 34].

A new anion RS^- coordinated to Co^{3+} ion determines its reduction, regenerating the Co^{2+} active site while yielding the dialkylsulfide. As indicated in literature, the dianion could also be formed by bonding the initial molecular oxygen to a single Co^{2+} site yielding a superoxo complex $Co^{3+}(L)_n(O_2)^-$, which through a slow reaction with another Co^{2+} site would generate a binuclear complex $Co^{3+}(L)_n(O_2)^{2-}Co^{3+}(L)_n$ if allowed by the dispersion of the complex species and the steric hindrances [3, 34].

Table 3

DEMERCAPTANIZATION OF TOLUENE IMPURIFIED BY C_2H_5SH (930 ppm) (0.015 MOLES C_2H_5SH /100g); 100g OF LIQUID SAMPLE CONTAINING 0.093 g C_2H_5SH + 0.35 g CATALYST; SWEETENING DURATION 15 MIN; T=25°C, AIR FLOW 5L·h^{-1}; CO CONCENTRATION VARIES IN THE RANGE 2.3 – 20 MICROMOLES·g^{-1}

Catalyst	Conversion of C_2H_5SH (%)	TOF min^{-1}
$[CoPcTS]^{4-}/HT_{2.3Co}$	91.4	116.1
$[CoCl_3P(C_6H_5)_3]^-/HT_{2.3Co}$	89.6	114.0
$[CoPcTS]^{4-}/HT_{4.5Co}$	96.5	61.1
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	94.8	60.1
$[CoCl_2BrP(C_6H_5)_3]^-/HT_{4.5Co}$	92.3	58.4
$[CoCl_3P(n\text{-}C_4H_9)_3]^-/HT_{4.5Co}$	89.0	56.4
$[CoCl_2BrP(n\text{-}C_4H_9)_3]^-/HT_{4.5Co}$	83.2	52.7
$[CoPcTS]^{4-}/HT_{9Co}$	98.8	31.3
$[CoCl_3P(C_6H_5)_3]^-/HT_{9Co}$	97.6	31.0
$[CoPcTS]^{4-}/HT_{13.5Co}$	99.4	21.0
$[CoCl_3P(C_6H_5)_3]^-/HT_{13.5Co}$	98.7	21.0
$[CoPcTS]^{4-}/HT_{20Co}$	99.6	14.0
$[CoCl_3P(C_6H_5)_3]^-/HT_{20Co}$	99.3	14.0

The results in table 3 prove that both the coordination of SR^- and oxygen as well as the modification of the oxidation state of cobalt may be sensibly affected by the nature and the structure of the ligands in the primary catalytic complex.

For the catalysts that gave the highest conversions of C_2H_5SH, e.g. $[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$ and $[CoPcTS]^{4-}/HT_{4.5Co}$ respectively, the influence of the transitional metal content in HTs supported samples on their activity in ethanethiol oxidative conversion to disulfide has been investigated. The obtained results are shown also in table 3.

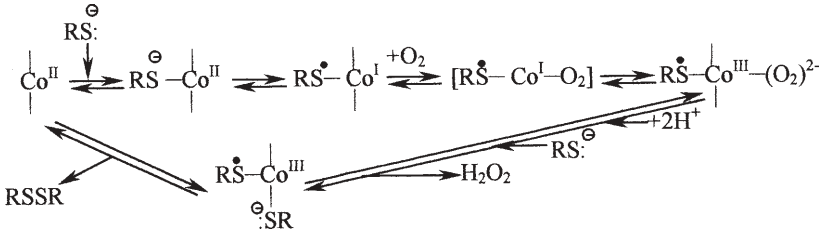
When the cobalt concentration increases in the range 2.3-20 micromoles Co per gram of catalyst, thiols conversions vary from 90 to 99.6%, the catalysts being very active while the differences of activity for the same concentration of metal are insignificant. However, it has been noticed that the catalyst effectiveness, expressed as TOF, decreases as the concentration of the cobalt complexes is increased. Since the aggregation and crystallization of the complexes on the support was not confirmed by the results of the XRD analyses, this behaviour may be related most likely to the blockage of the galleries at high concentration of Co complexes, which induces a decrease in the number of accessible active sites. These processes taking place especially when the softening is carried out in solution, in homogeneous environment are less obvious when the complex molecules are anchored either in a zeolite supercage or by their intercalation in pillared clays since in these cases the migration is partially hindered [13, 35]. Considering both the catalyst effectiveness and the conversion level, it may be concluded that the catalyst containing 4.5 micromoles Co per gram presents the best performances, allowing ca. 95% conversion of the ethanethiol at 60min^{-1} TOF.

Therefore, this catalyst has been tested also in the demercaptanization of toluene contaminated with identical concentrations of different thiols (0.015 moles %). The results are presented in table 4.

It has been noticed that the order of reactivity in thiols oxidation to alkyldisulfides decreases in the following order: primary thiol > secondary thiol > tertiary thiol. In the above sequence, thiophenol is placed between the secondary and tertiary thiols, respectively.

The catalytic activity of both catalysts is very high (95-96% conversion) and practically equal for the oxidation of ethanethiol. Significant differences between the activities of the catalysts appear in what concerns the oxidation of the undesirable thiols: secondary thiols, tertiary thiols and thiophenol, respectively. The catalyst $[CoPcTS]^{4-}$/HTs is a little bit more active than $[CoCl_3P(C_6H_5)_3]^-$/HTs. Taking into account that the duration of the sweetening was short (15 min) and the initial concentration of thiols excedded 1000 ppm, we appreciate that the activity of the two catalysts is high enough. Similar behaviours in the series of alkanethiols have been also reported in the presence of transitional metal phtalocyanines in homogeneous conditions [15].

For both catalysts, the variation of the catalytic activity as a function of the reaction time under the experimental conditions employed has the same trend to reach a constant level in the case of toluene containing traces of ethanethiol as well as in the case of toluene impurified



Scheme 1 Mechanism of oxidative demercaptanization

Table 4

DEMERCAPTANIZATION OF TOLUENE IMPURIFIED BY DIFFERENT MERCAPTANS RSH (0.015 MOLES RSH /100g); 100g OF LIQUID SAMPLE CONTAINING 0.015 MOLES RSH + 0.35 g CATALYST; SWEETENING DURATION 15 MIN; T=25°C, AIR FLOW 5L·h^{-1}; CO CONCENTRATION 4.5 MICROMOLES·g^{-1}

Catalyst	RSH	Initial Concentration of RSH ppm (g/g)	Conversion of C_2H_5SH (%)	TOF min^{-1}
$[CoPcTS]^{4-}/HT_{4.5Co}$	C_2H_5SH	930	96.5	61.1
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	C_2H_5SH	930	94.8	60.1
$[CoPcTS]^{4-}/HT_{4.5Co}$	*i*-C_3H_7SH	1140	78.9	50.0
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	*i*-C_3H_7SH	1140	76.1	48.3
$[CoPcTS]^{4-}/HT_{4.5Co}$	*t*-C_4H_9SH	1350	55.3	35.0
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	*t*-C_4H_9SH	1350	49.6	31.4
$[CoPcTS]^{4-}/HT_{4.5Co}$	C_6H_5SH	1650	69.5	44.0
$[CoCl_3P(C_6H_5)_3]^-/HT_{4.5Co}$	C_6H_5SH	1650	61.7	39.1

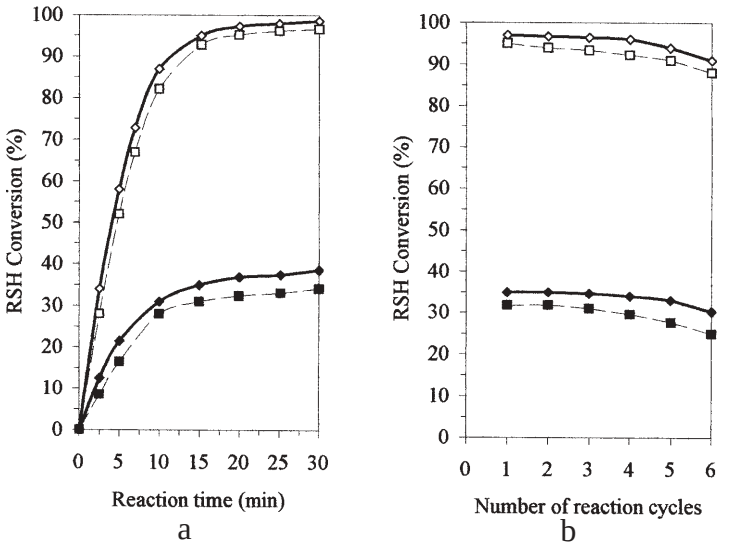


Fig. 4. Variation of RSH conversion as a function of reaction time (a) and of the number of reaction cycles (b). Catalysts: $[CoPcTS]^{4-}/HT_{4.5Co}$ (solid line, ◇ - conversion of C_2H_5SH, ♦ - conversion of *t*-C_4H_9SH); $[CoCl_3PC_6H_5)_3]^-/HT_{4.5Co}$ (dotted line, □ - conversion of C_2H_5SH, ■ - conversion of *t*-C_4H_9SH)

with *t*-butanethiol, even if the maximum level of the conversion reached in each case is different (fig.4a).

The results of cyclic experiments involving several sequences reaction-regeneration are shown in figure 4b.

In each reaction cycle the same catalyst sample has been used. The catalyst has been separated by decantation, washed with acetone and dried before being used in the next reaction cycle. In each cycle, 100g of fresh liquid fraction contaminated with ethanethiol and *t*-C_4H_9SH respectively, was used.

For both catalysts, a slight trend of decrease in the activity after the first six reaction cycles is noticed. This trend is more evident for the flow contaminated with *t*-C_4H_9SH. This fact may be related to the presence of low soluble dialkylsulfides, which are accumulated in the catalytic mass as well as to a partial neutralisation of the base sites of the hydrotalcite by the thiols that have a slightly acid character.

Conclusions

Based on the above-presented results it may be concluded that besides Co-ftalocyanines complexes there are other Co-complexes such as trihydrocarbyl-phosphinetrihalocobaltate $[R_3PCoHal_3]^-$ which are active catalysts for demercaptanization when it is immobilised

on HTs. Their activity is sensibly influenced both by the nature of the halide ion, the trihydrocarbylphosphine ligands and perhaps by their different affinity for the inclusion of water molecules in their coordination sphere. The catalytic activity for the demercaptanization is also influenced by the oxidation susceptibility of the thiols.

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