Epoxidation of Cyclohexene With H_2O_2 and Acetonitrile Catalyzed by Mg–Al Hydrotalcite and Cobalt Modified Hydrotalcites

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Abstract The paper presents a comparison between the results obtained for cyclohexene epoxidation in the presence of base catalysts: $Mg_{0/75}Al_{0.25}$ -hydrotalcite (HT), the corresponding mixed oxide (CHT), the reconstructed hydrotalcite (RHT), a hydrotalcite containing cobalt in the brucite-type layer ((Co-Mg_{0.75})Al_{0.25})) and one containing cobalt complex-species supported on HT carrier (Co-complex/HT). The selective conversion of cyclohexene to the corresponding epoxide is closely related to the base strength of the catalysts.

Keywords Cyclohexene epoxidation · Mg–Al–HTlc · MgAl mixed oxides · Reconstructed hydrotalcite · Co-HTlc

1 Introduction

Selective epoxidation of olefinic compounds is one of the important steps in organic synthesis of fine chemicals,

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National Institute for Lasers, Plasma and Radiation Physics, P. O. BOX Mg-27, Măgurele, Bucharest, Romania since by ring opening reactions, epoxides are directly transformed into a wide array of compounds. Among various oxidation agents the use of hydrogen peroxide deserves a special attention as an easy to handle and clean oxidation agent which can be reduced only to water by the end of the process. According to Payne's works [1, 2] by combining an oxidant such as H_2O_2 and a nitrile in the presence of a base catalyst, the nitrile is converted to amide via a peroxycarboximidic acid intermediate which serves as a terminal oxygen donor.

Recent studies performed by Kirm et al. [3] showed that solid bases such as mixed oxides obtained from Mg/Al hydrotalcite-like precursors can act as heterogeneous catalysts for the epoxidation of styrene, using a combined oxidant of hydrogen peroxide and acetonitrile in the presence of acetone and water as solvents. The authors concluded that several factors such as the Mg/Al ratio, the presence of the pure hydrotalcite phase in the mixed oxide samples, the reconstruction rate of the hydrotalcite-like phase during the reaction, and the addition of water, play an important role in the selective epoxidation of styrene.

Therefore, one of the goals of this work has been to provide new insights on the role played by the hydrotalcitelike phase and the impact of the reconstruction through the "memory effect" presented by hydrotalcite-like materials on the selectivity of the transformation of cyclohexene to cyclohexane epoxide. To do so, the catalytic activities of a parent hydrotalcite (HT), have been compared with those of the corresponding mixed oxide (CHT) and the reconstructed hydrotalcite obtained through rehydration of the mixed oxide (RHT) under identical reaction conditions. In order to select the operational parameters the effects induced by the solvents and the presence of the acetonitrile on the catalytic performances of the parent hydrotalcite have been investigated. Another aspect considered in the elaboration of this work is that a significant number of researches concern the partial oxidation of the organic substrates with H_2O_2 , [4–9], alkylhydroperoxides or peroxyacids [10–12] using transition metal complexes as catalysts. The use of these catalysts in homogeneous catalytic conditions is inconvenient because the catalyst cannot be recovered and reused.

The second cobalt-modified hydrotalcite, containing the same amount of cobalt $(3.5 \times 10^{-4} \text{ mol } \text{Co} \cdot \text{g}^{-1})$ has been prepared using as cobalt source an admixture of bis-triphenylphosphine-dichlorocobalt (II) $\text{Co}[P(C_6H_5)_3]_2\text{Cl}_2$ (A) and benzyltriphenyl phosphonium—tetrachlorocobaltate $[C_6H_5\text{CH}_2P(C_6H_5)_3]_2^+[\text{CoCl}_4]^{2-}$ (B) which has been obtained according to the reaction:

$$CoCl_{2} + 2P(C_{6}H_{5})_{3} + C_{6}H_{5}CH_{2}Cl \rightarrow 0.5Co\left[P(C_{6}H_{5})_{3}\right]_{2}Cl_{2} + 0.5\left[C_{6}H_{5}CH_{2}P(C_{6}H_{5})_{3}\right]_{2}^{+}[CoCl_{4}]$$
(1)

The current trend is to immobilise the complex on a host support such as zeolites [13–16], macroporous carbon [17], polymers [12, 18, 19], or hydrotalcites [20–22].

Based on this state of the art, the second goal of this work was to highlight an eventual synergetic effect of the transition element and the base function of the HT solid for the selective epoxidation of cyclohexene. Therefore, the performances of cobalt modified hydrotalcites with cobalt introduced in the brucite-type layer or simply supported as complex species on a hydrotalcite carrier have also been investigated.

2 Experimental

2.1 Catalysts Preparation

The Mg_{0.75}Al_{0.25} hydrotalcite (HT) was synthesized at pH 10 under low supersaturation conditions, using Fluka analytical grade Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Na₂CO₃ and NaOH as raw materials, according to the procedure described in detail earlier [23, 24].

The CHT mixed oxide derived from HT was obtained through the calcination of the dried HT at 460 °C during 18 h under nitrogen flow.

The reconstructed hydrotalcite structure (RHT) was prepared by rehydration of CHT which was immersed in decarbonated water for 24 h at 25 °C under nitrogen. Then the sample was dried at 25 °C under vacuum (10^{-2} torr). All samples were kept under nitrogen blanket before being used.

One cobalt modified hydrotalcite $(Co-Mg)_{0.75}Al_{0.25}$ was obtained by coprecipitation using the method previously described for HT synthesis in which a part of $Mg(NO_3)_2 \cdot 6H_2O$ was substituted by $Co(NO_3)_2 \cdot 6H_2O$ in order to correspond at $(Mg^{2+} + Co^{2+})/Al^{3+} = 3$ molar ratio and a concentration of 3.5×10^{-4} mol $Co \cdot g^{-1}$ in the final catalyst.

The reaction (1) was performed under nitrogen at 60 °C during 6 h using a mixture of 0.02moles triphenylphosphine (P(C₆H₅)₃) with 0.01moles benzylchloride C₆H₅CH₂Cl and 0.01 moles CoCl₂·6H₂O solved in n-butanol. Then the solvent was evacuated under vacuum and the solid bright blue crystals were separated under nitrogen and recrystal-lized from n-butanol. The product is a mixture of A and B cobalt complexes since in the case of chlorine ionic complexes the compound benzyltriphenyl phosphonium-triphenyl phosphine-trichlorocobaltate [C₆H₅CH₂P C₆H₅)₃]⁺ [(C₆H₅)₃PCoCl₃]⁻ could not be obtained by this procedure [25].

An acetone solution of the cobalt precursor (Co concentration 6.5×10^{-3} mol.L⁻¹) was contacted with the HT support previously dried under vacuum during 24 h at 25 °C. The resulting solid was filtered, washed three times with acetone, then with benzene and finally dried under vacuum (10^{-2} torr) at 25 °C. The obtained catalyst was stored under nitrogen.

2.2 Catalysts Characterization

The metal content in all catalysts has been determined by AAS spectroscopy.

The XRD patterns were collected on a PANalytical X'Pert MPD theta-theta system in continuous scan mode (counting 2 s per 0.02 2θ) ranging from 5° to 72° 2θ , using a Ni filter ($\lambda = 0.15418$ nm), and a curved graphite monochromator. Data were analyzed using PANalytical X'Pert HighScore Plus software package.

The as-synthesized complex and the catalysts were characterized by DR–UV–Vis in the range of 210–915 nm. The spectra have been recorded with a SPECORD 80 UV–VIS spectrometer with an integration sphere coated with MgO taken as reference.

A Micromeritics ASAP 2020 apparatus was used in order to evaluate the specific surface area of the samples by nitrogen adsorption after degassing the samples in situ at 70 $^{\circ}$ C for 24 h.

The surface base sites of the catalysts were determined using a method similar to the one developed by Parida and Das [26] on the basis of the irreversible adsorption of organic acids with different pK_a , e.g. acrylic acid, $pK_a = 4.2$ and phenol $pK_a = 9.9$. The amount of adsorbed phenol is related to the number of strong surface base sites while the amount of adsorbed acrylic acid is related to the total number of base sites. The number of weak base sites is given by the difference between the amount of adsorbed acrylic acid and the adsorbed phenol. Before base sites measurement, all catalysts were thoroughly degassed under vacuum at room temperature. Catalyst samples (0.05 g)were introduced in brown sealable bottles and 10 mL of freshly prepared solution containing the organic acid (e.g. phenol and acrylic acid, respectively) in methylcyclohexane was added. Afterwards, the bottles were sealed and were shaken for 2 h at 30 °C. It was assumed that the interaction of the solids with atmospheric CO_2 and water was negligible since their exposure to atmosphere was limited to the weighing period. The time required for the system to reach the equilibrium at constant temperature was checked for each solid and it was never longer than 1 h.

After 2 h the concentration of the acid remaining in solution was determined spectrophotometrically at λ_{max} (e.g. 276.5 nm for phenol, and 231.5 nm for acrylic acid) using the calibration curves absorption versus acid concentration in the range where the Lambert–Beer law is fitted. The amount of adsorbed phenol and adsorbed acrylic acid, respectively, is given by the difference between the amount of the respective acid introduced in the test and the amount that remained in solution after 2 h. The reproducibility of the spectrophotometric method was checked experimentally, and the measurements were repeated 2–3 times. The relative error was approximately 5%.

2.3 Catalytic Tests

The activity and selectivity of the catalysts were tested in the oxidation of cyclohexene with hydrogen peroxide using acetonitrile as reductant. The reactions were performed in a stirred flask (500 mL) at 60 °C, for 5 h reaction time. In a typical experiment cyclohexene (4 mmol) and acetonitrile (32 mmol) were dissolved in 20 mL of solvent. (two types of solvents have been used: (a) methanol and (b) equivolumic admixture of water and acetone). All reagents were freshly distilled. In all reactions the catalyst concentration was 0.3% in the reaction admixture (w/w).

The reaction was monitored hourly using a GC K072320 Thermo Quest Chromatograph equipped with a FID detector and a capillary column of 30 m length with DB5 stationary phase. The oxidation products were identified by comparison with a standard sample (retention time in GC). The reaction products were identified also by mass spectrometercoupled chromatography, using a GC/MS/MS VARIAN SATURN 2100 T equipped with a CP-SIL 8 CB Low Bleed/ MS column of 30 m length and 0.25 mm diameter.

3 Results and Discussion

3.1 Characterization

3.1.1 XRD and Textural Analyses

The XRD patterns of the parent hydrotalcite HT and reconstructed hydrotalcite RHT (Fig. 1a) exhibit the typical pattern of a layered double hydroxide material (JCPDS file 70-2151), indexed in a hexagonal lattice with a R3mrhombohedral symmetry, while the pattern of the parent CHT support (Fig. 1b) is that of a mixed oxide Mg(Al)O with MgO-periclase structure (JCPDS file 45-0946, indexed in a cubic symmetry. The XRD patterns of the cobalt containing samples are similar to those of the Cofree samples with no extra peaks originating from crystalline cobalt species, indicating a high dispersion of cobalt on the supports. The data in Table 1 show that no substantial modification of the *a* and *c* parameters were observed for Co-complex/HT which suggests that, more likely, the cobalt complexes covered preferentially the outer surface and in a very low amount the interlayer space, adopting flat-lying position.

In the case of $(Co-Mg)_{0.75}Al_{0.25}$ the isomorphous substitution of Mg^{2+}/Al^{3+} by Co^{2+}/Co^{3+} was not to evidenced by any variation of the *a* parameter value due to the low amount of Co as well as to the very good match of the ionic radii of Co^{2+} and/or Co^{3+} with Mg^{2+} and/or Al^{3+} .

The results of the textural analysis presented in Table 1 showed that the hydrotalcite-like materials have similar specific surface areas in the range $125-138 \text{ m}^2/\text{g}$. The modification with cobalt leads to a small decrease of the pore size compared to the parent HT. Both the surface area and the pore size of the reconstructed hydrotalcite were sensibly lower than those of the parent HT.

3.1.2 Characterization by DR-UV-Vis

The DR–UVVis spectra of cobalt containing catalysts as well as those of the neat complexes are presented in Fig. 2.

The spectrum of $(\text{Co-Mg})_{0.75}\text{Al}_{0.25}$ catalyst presents only the features characteristic for Co cation species in octahedral symmetry, consistent with the structure of the brucitetype layer [27, 28]. The presence of the bands at 419 and





Table 1 Structural and textural properties of the catalysts

Catalysts	XRD analysis			Texture analysis			
	Unit cell parameters		Crystallite	BET surface	Pore	Vol. ads. (cm ³ /g)	
	a (nm)	c (nm)	sizes (nm)	area (m²/g)	size (nm)		
HT	0.3056	2.3185	9.1	131	18.9	0.6220	
Co-complex/HT	0.3055	2.3232	9.3	138	15.5	0.5351	
(Co-Mg) _{0.75} Al _{0.25}	0.3056	2.3154	8.7	125	16.7	0.5562	
RHT	0.3055	2.3181	16.3	3.2	6.7	0.0054	
CHT ^a	0.4181		3.2	250	14.4	0.8990	

^a Cubic structure

517 nm indicates that some of Co (II) ions were oxidized to Co(III). This partial oxidation of Co(OH)₂ to Co(OH)₃ (or CoOOH) in basic media was also reported by Leroux and Zheng.[28, 29] who showed that the oxidation is thermodynamically very favorable at low oxygen pressure which is reached during the aging period of the precipitate.

The spectrum of the solid admixture of Co-complexes shows the characteristics specific for distorted tetrahedral symmetry of Co (II) species with very intense bands in the region of d-d transitions [25, 27, 30, 31]. Meanwhile for the complex solved in acetone (that was used as catalyst in homogeneous conditions), the intense bands from the region of charge transfer up to 300 nm are absent and only the bands corresponding to d-d transitions of the complex can be noticed. The DR–UV–Vis spectrum of Co-complex/HT, reveals that upon impregnation the structures of the cobalt precursor complexes are altered, and the cobalt species are found mainly in octahedral symmetry. The presence of the traces of tetrahedral coordinated Co(II) species is indicated by the shoulder of the band at 705 nm (v_2), while the band at 664 nm indicates the presence of Co(II) in octahedral symmetry. Some of the bands corresponding to ligand to metal charge transition (LMCT) are overlapped by the bands characteristic for the tetrahydrocarbylphosphonium cation around 300 nm [32]. The bands at 521 and 610 nm indicate the presence of some traces of Co (III) species with octahedral coordination. The oxidation of Co(II) to Co(III) may occur due to the base character of the support during the impregnation.



Fig. 2 DR-UV-Vis spectra of Co-containing catalysts

3.1.3 Determination of the Surface Base Sites

Taking into account that the determination of the base sites using TPD of CO₂ can be applied only for the calcined hydrotalcite sample (e.g. CHT) and cannot be applied to the dried hydrotalcite-type samples, it has been preferred to apply the method based on the titration of the surface base sites at 30 °C in order to compare the basicity of all the catalysts investigated in this study. Acids with different pK_a , such as acrylic acid, $pK_a = 4.2$ and phenol $pK_a = 9.9$

Table 2 Distribution of base sites for the investigated catalysts

have been used for this purpose. This type of method presents the advantage that it may be used to determine the base sites of solids that cannot undergo calcinations without altering their structure.

Even if the results obtained using this method should not be considered as absolute values since the number of base sites titrated depends also on the accessibility of the organic acid to the base sites (which is related to the dimensions of the pores in the solid) the method allows a relative classification of the catalysts as a function of the number of accessible base sites.

It has been assumed that the results obtained using the titration method may be correlated to the results of the catalytic activity tests since the molecular dimensions of phenol are comparable to those of the largest molecular dimensions of the participating molecules (e.g. cyclohexene and cyclohexane epoxide) in the investigated catalytic oxidation process.

The results of these investigations as presented in Table 2 show that the catalyst CHT has the highest number of total base sites. This fact is rather surprising since by consideration of their theoretical formulae one would expect that the calcined solid has a lower number of base sites compared to HT and RHT. When comparing the results obtained by titration with the theoretical values of the base sites numbers (e.g. moles anions per gram of catalyst) calculated using their chemical formulae it seems that the titration method allows the determination of ca 15–22% of the total of base sites, probably due to the fact that only the base sites on the external surface of the catalyst are titrated. Therefore it seems that the larger number of total base sites for CHT is a consequence of its larger surface area.

The values of the total number of base sites for RHT and HT vary in the order indicated by the theoretical calculations, while respecting the above statement that only the accessible base sites are titrated. The hydroalcite containg Co in the brucite type layer, $(Co-Mg)_{0.75}Al_{0.25}$, has a slightly lower basicity expressed as mmoles/g compared to HT. This fact should be expected since the molar weight of $(Co-Mg)_{0.75}Al_{0.25}$ is slightly higher than that of

Catalysts	Total number of base sites	Distribution of base sites			
	(mmol acrylic acid/g catalyst)	Strong base sites (mmol phenol/g catalyst)	Weak and medium strength base sites (mmol/g catalyst) ^a		
HT	6.73	0.26	6.47		
Co-complex/HT	4.46	0.23	4.23		
(Co-Mg) _{0.75} Al _{0.25}	6.58	0.24	6.34		
RHT	7.21	0.34	6.87		
CHT	8.36	0.38	7.98		

^a Weak and medium strength base sites = total number of base sites - strong base sites)

 $Mg_{0.75}Al_{0.25}$, and consequently the number of mmoles per gram of catalyst will be lower.

The lowest number of base sites is obtained for Cocomplex/HT and it may be a consequence of a screening of the base sites by the Co-complex.

3.2 Results of Catalytic Tests

The catalysts have been tested for the oxidation of cyclohexene with hydrogen peroxide in the presence of acetonitrile as reductant agent using either an admixture wateracetone (1:1 volume ratio) or methanol as solvent. The reaction path adapted from the work of Kirm et al. [3] is presented in Scheme 1.

The results presented in Fig. 3 show that the presence of both the acetonitrile and the solid base catalyst are absolutely necessary for the reaction.

When both the acetonitrile and the catalyst are absent from the reaction mixture or when the acetonitrile was added to the reaction mixture in the absence of the catalyst, the conversions of cyclohexene are limited to 20% and the values of the yield to cyclohexane epoxide are low (less than 5%) (Fig. 3a, b).

The reaction performed with cyclohexene and H_2O_2 in the presence of the hydrotalcite-like catalyst without adding acetonitrile, leads to high conversions of cyclohexene (e.g. 88%). However the process has a poor selectivity and allows a wide range of byproducts to be obtained besides the cycohexane epoxide for which the yield is only 10%.

In the reactions performed under identical conditions in the presence of the catalyst HT, it has been noticed that the values of the conversion and selectivity to cyclohexane epoxide depend on the molar ratio cyclohexene: H_2O_2 as well as on the nature of the solvent employed.

The results show that an excess of hydrogen peroxide is favorable to obtain cyclohexene conversions over 90% with a yield to epoxide over 80% after 5 h reaction time.

Even if at short reaction time in water–acetone solvent the conversion and the yield to epoxide are lower than those obtained in methanol solvent, after 5 h reaction time they reach almost the same value. Taking into account the



Scheme 1 Peroxidation of cyclohexene with hydrogen peroxide on base catalysts in the presence of CH_3CN

high toxicity of methanol it would be preferable to use the admixture water-acetone as solvent since it implies a lower amount of organic solvent and it is more eco-friendly.

In the reactions performed in the presence of HT catalyst while using CH₃CN reductant the best results are obtained after 5 h reaction time in acetone–water solvent at a molar ratio cyclohexene: $H_2O_2 = 1:8$.



Fig. 3 Temporal variation of the conversion of cyclohexene (a) and yield to epoxide (b) during the oxidation of cyclohexene with H_2O_2 at 60 °C, solvent water–acetone 1:1 vol./vol — solvent methanol—square molar ratio cyclohexene: H_2O_2 1:8; catalyst HT, reductant CH₃CN *filled circle* molar ratio cyclohexene: H_2O_2 1:4 catalyst HT, reductant CH₃CN *triangle* molar ratio cyclohexene: H_2O_2 1:8 catalyst HT, without reductant *open circle* molar ratio cyclohexene: H_2O_2 1:8 without catalyst, without reductant, *multiplication symbol* solvent water–acetone 1:1 vol./vol; molar ratio cyclohexene: H_2O_2 1:8 without catalyst, with reductant CH₃CN

As it may be seen from the results displayed in Fig. 4, in the reactions performed in the presence of HT catalyst while using CH_3CN reductant in acetone–water solvent



Fig. 4 Conversion of cyclohexene (**a**) and selectivity to cyclohexane epoxide (**b**) after oxidation with H_2O_2 during 5 h reaction time at 60 °C molar ratio cyclohexene: $H_2O_2 = 1.8$; solvent : water-acetone 1:1 vol./vol, *filled diamond* HT; Open diamond (Co-Mg)_{0.75}Al_{0.25}; *filled circle* Co-complex/HT; *multiplication symbol* Co-complex; *open circle* CHT; *filled triangle* RHT

(molar ratio cyclohexene: $H_2O_2 = 1:8$), the conversions and yields to cyclohexane epoxide obtained while using HT, the corresponding mixed oxides CHT, or the reconstructed hydrotalcite RHT as catalysts are high and their values are comparable.

The above-mentioned catalysts are solids with base character, their base strength varying in the following order: CHT > RHT > HT as it was shown in several previous publications [33, 34] and confirmed by our results of the base sites determinations as presented in Table 2.

Corma et al. showed that pure MgO possesses strong base sites consisting of O^{2-} while CHT contains surface sites with different base strength such as OH^{-} groups (low), M–O pair (medium) and O^{2-} (strong) [33].

The rehydrated sample RHT contains OH^- ions in the interlayer which act as Brönsted base sites with a stronger basicity than CO_3^{2-} ions located inside the parent hydrotalcite structure [35].

These three catalyst samples differ neatly not only by their base strength but also by their specific surface areas and porous structures, as it may be seen from the data presented in Table 1. In some of our previous publications [34] as well as in Takehira's work [36] it has been showed that HT and RHT, respectively, have different morphology even if both samples exhibit a hydrotalcite-like structure. The change of morphology in the RHT sample appears both at the edge of crystals where worm-like structures are formed as well as defects on the plate that were evidenced by TEM [34]. Since the worm-like structures formed at the edge of the crystals block the access to the interlayer there is a dramatic decrease of the BET surface area of RHT compared to the HT sample. Taking into account this aspect it may be assumed that the base sites are preferentially located on the external surface of the solid.

To what concerns the catalytic activity of CHT which one would expect to be much higher due to its larger surface area and number of base sites, the presence of water used as solvent in the reaction mixture may induce the partial reconstruction of the hydrotalcite structure when contacted to CHT leading to a solid more similar to RHT or HT. This fact may explain the similarity of the results obtained when using RHT, HT and CHT catalysts even if the fresh CHT has a much higher surface area. Therefore, the small differences of activities and selectivities obtained in the reactions performed with these three catalysts, suggest that in the case of the investigated reaction, the most important role is played by their acid–base character and not particularly by their porous structure or by the morphology of the catalyst.

The experiments aimed at highlighting an eventual synergetic effect of cobalt and the base function of the HT solid for the investigated reaction have been performed using the Co modified hydrotalcite-like compounds as catalysts for the oxidation of cyclohexene with hydrogen

Catalyst	Distribution of by-products (%) ^a							
	Cyclohexenol	Cyclohexane-1,2-diol	Cyclohexanone	Cyclohexenone	Adipic acid	Others		
HT	_	-	1.1	4.5		5.2		
Co-complex homogeneous catalysis	4.7	23.5	_	-	41.8	20.4		
Co-complex/HT	2.0	7.9	_	3.0	7.8	11.2		
CHT			0.3	0.6		0.2		
RHT		0.5	1.0		0.3			
(Co-Mg) _{0.75} Al _{0.25}			1.2	1.8		0.9		

Table 3 Distribution of the reaction by-products at cyclohexene oxidation with hydrogen peroxide using CH_3CN reductant, water-acetone 1:1 vol/vol solvent after 5 h reaction time at 60 °C for the investigated catalysts

^a The balance up to 100% is cyclohexane epoxide

peroxide under the selected above-mentioned reaction conditions. Their catalytic performances have been compared to those of the unmodified hydrotalcite as well as to those of a cobalt complex catalyst used under homogeneous catalysis conditions.

The test reaction under homogeneous catalysis conditions has been performed using cyclohexene, H_2O_2 , acetonitrile and the cobalt complex catalyst solved in the acetone–water solvent without adding the hydrotalcite. The results are also displayed in Fig. 4.

Under homogeneous catalysis conditions, both the conversion and the selectivity to cyclohexane epoxide after 5 h reaction time has low values e.g. 40 and 10.56% respectively as it may be seen in Fig. 4. Under the influence of the powerful oxidizing agent the color of the solution owed to the presence of the solved cobalt complex turns from blue to green due to the oxidation of the cobalt complexes by the hydrogen peroxide.

From Fig. 4 it may also be seen that compared to the activity of the parent HT, after 5 h reaction time the activity of $(Co-Mg)_{0.75}Al_{0.25}$ is practically unmodified. Thus it may be concluded that the effect of the Co^{2+} ions partially substituting Mg^{2+} in the brucite-type layer is not significant. This fact is also confirmed by the determination of structural and textural data (Table 1) and the number of base sites presented in Table 2. However, it is interesting to notice that at the beginning of the catalytic test $(Co-Mg)_{0.75}Al_{0.25}$ is more active than HT. This proves its bifunctional character due to the presence of both base sites related to the hydrotalcite structure and redox sites related to the presence of Co.

The hydrotalcite-like catalyst modified by impregnation with cobalt complex leads to a conversion that is 13% lower and a yield to cyclohexane epoxide lower by 31% compared to those obtained with the un-modified hydrotalcite. The ability of Co^{2+} to modify both its oxidation state to Co^{3+} as well as its coordination number from 4 to 6, increases the possibility to catalyze competitive parallel reactions leading to the formation of by-products. These results suggest that following the impregnation, some of the base sites of the

hydrotalcite are affected by the interaction with the cobalt complex species. This fact is also confirmed by the data presented in Table 2, which show the lower number of weak base sites in Co-complex/HT. Moreover the properties which determine the selective catalytic activity of the cobalt species, namely their composition, structure and symmetry are altered by the influence of the hydrogen peroxide as it is the case under homogeneous catalysis conditions and it can be seen in the DR–UV–Vis spectra.

The analysis of the by-products obtained during the reactions performed with cobalt complex supported on HT as well as the modest yield to cyclohexane epoxide complete the finding that similar to the test under homogeneous catalysis conditions using only cobalt complexes as catalyst without the hydrotalcite, the reaction is non-selective with respect to cyclohexane epoxide formation.

In the latter case the absence of the base solid in the reaction mixture leads the chemical transformation mainly to form 1,2-cyclohexanediol and adipic acid (the selectivities towards these products being 24 and 42%, respectively as it may be seen in Table 3).

In the reaction catalysed by the cobalt complex supported on HT, the selectivities to these by-products are lower probably due to the screening of some base sites of the support.

The use of the cobalt-free hydrotalcites HT, CHT and RHT for this reaction leads to the selective formation of cyclohexeneperoxide by the epoxidation of cyclohexene with high conversions. The by-products cyclohexanone, cyclohexenone and unidentified by-products are formed to low extent while the presence of the base sites in the hydrotalcite hinders strongly the formation of 1,2 cyclohexanediol by opening of the oxirane ring.

4 Conclusions

Hydrotalcite catalysts, reconstructed by memory effect and their corresponding mixed oxides have been studied in the selective oxidation of cyclohexene with H_2O_2 in the presence of acetonitrile as reductant agent. The activity and selectivity of the catalysts depends on the molar ratio cyclohexene/ H_2O_2 as well as on the nature of the solvent used.

Correlating the results of the determination of surface base sites and those obtained in the catalytic tests leads to the conclusion that the highest catalytic activity is obtained for the samples exhibiting the highest number of weak and medium strength base sites. Therefore the base strength of the catalysts has been proven to be essential for the selective conversion of cyclohexene to the corresponding epoxide.

Modifying the hydrotalcite structure with low concentrations of Cobalt ions (ca. 2% w/w) localized in the brucite-type layer does not change sensibly the performances of the catalyst compared to the un-modified hydrotalcite.

The catalyst modified with the same concentration of cobalt using cobalt complexes with triphenyphosphine and chlorine ligands as cobalt source lead to interactions between the complex species and some of the base sites of the support which affect negatively their activity and selectivity.

The differences between the performances of $(Co-Mg)_{0.75}Al_{0.25}$ prepared by co-precipitation and Cocomplex/HT obtained by impregnation suggest that the hydrogen peroxide alters by oxidation the Co-species grafted to the base carrier, leading also to a leaching of the complex during the catalytic test. The modification of the composition and structure of these Co-complex species is reflected by the different activity and selectivity compared to $(Co-Mg)_{0.75}Al_{0.25}$ that has Co^{2+} ions in the brucite-type layer. Researches are in course using air or pure oxygen as oxidant in order to avoid the destruction of the cobalt complex.

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