



Epoxidation of cyclohexene with O₂ and isobutyraldehyde catalysed by cobalt modified hydrotalcites

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ABSTRACT

The paper presents a comparison between the catalytic performances of cobalt modified hydrotalcites obtained from different cobalt precursors in the epoxidation of cyclohexene using molecular oxygen, isobutyraldehyde as reductant, at 25 °C and 1 atmosphere pressure of oxygen in acetonitrile as solvent. Two different types of cobalt containing catalysts were prepared: (i) a hydrotalcite-like compound containing cobalt in the brucite type layer, CoMg/Al, and (ii) three catalysts obtained by impregnation of the as-synthesized hydrotalcite support (HT) with CoCl₂, bis-triphenylphosphine-dichlorocobalt (II) Co[P(C₆H₅)₃]₂Cl₂, (A), and an admixture of complexes (AB) containing bis-triphenylphosphine-dichlorocobalt (II) Co[P(C₆H₅)₃]₂Cl₂ (A) and benzyltriphenyl phosphonium-tetrachlorocobaltate [C₆H₅CH₂P(C₆H₅)₃]₂⁺[CoCl₄]₂⁻ (B). The names of these catalysts have been abbreviated as CoCl₂/HT, A/HT and AB/HT. The catalysts were characterized by chemical analyses, DR-UV-vis, DRIFTS, XRD, EDX and texture measurements. The most active and selective catalyst was AB/HT. A linear correlation between the ratio Cl/Co in the resulting solids and the yield to epoxide has been established. For AB precursor the effect of the support has been also investigated using as carriers the mixed oxide CHT derived from the calcination of the parent hydrotalcite, and the reconstructed hydrotalcite RHT obtained by rehydration of CHT.

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1. Introduction

The epoxidation of olefins has attracted much attention since epoxides are key intermediates in organic synthesis of fine chemicals [1–4].

In the recent years, many efforts have been dedicated to the development of routes for the preparation of epoxides using efficient catalysts under environmental “friendly” conditions [3,5,6].

Several redox active metallo-porphyrins [3,4,7–9,10], phthalocyanines and other metal complexes such as transition metal β-diketonate [11–13], oxovanadium (IV) complex [14], metal – Salen or Accacen [13,15,16], metal complex with 8-hydroxyquinoline [16] etc., can act as catalysts for oxidation of olefins with H₂O₂, ROOH or molecular oxygen. The exploitation of these metal complexes in homogeneous catalytic conditions is inconvenient because they could not be recovered and because their activities are limited to a few catalytic turnovers.

The deactivation of the homogeneous metal complexes is partially due to the interaction with high reactive oxidizing agents like H₂O₂, alkylperoxides or peroxyacids; it also arises from the formation of a peroxo-bridged dinuclear complex of the type [LMe^{II}O₂Me^{II}L_n] which is unable to bind and to activate another oxygen molecule [17,18].

The immobilization of the complex into the host solid matrix appears to be particularly effective in suppressing the dimerization of oxo-intermediates or in the inactivation due to the oxidation of the active complex species.

The heterogeneization of the metal complexes by chemical bonding to a support leads to an increase of their stability and makes easier the separation of the catalyst after reaction in order to be reused. For this purpose, a variety of supports have been used, such as: zeolites [19–23], polymers [16,24,25], nanoporous carbon [26] or hydrotalcites [18,27–32].

Employing oxidant reagents which maximize atom efficiency is also a key goal in oxidation reactions.

Molecular oxygen is one of the most interesting oxidizing agents to be used as an alternative to NaOCl, H₂O₂, alkylperoxides or peroxyacids. Some recent studies have reported on transitional metal complexes deposited on hydrotalcites as new efficient catalysts

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in the aerobic epoxidation of olefin with isobutyraldehyde, as the reductant under mild conditions [11,26,28,33].

The aim of this work was to study the behaviour of some Co-modified hydrotalcite-like catalysts during cyclohexene epoxidation with molecular oxygen in the presence of isobutyraldehyde. The activity and selectivity of the catalysts which incorporated the same amount of cobalt but were prepared by different techniques using different cobalt precursors was investigated. The catalytic performances of the solids were correlated to the effect induced by different types of ligands, the location of the catalytic active species in correlation with the morphology, and pore structure of the host supports. The effect of the reactivity of the substrate was also studied using different linear and cyclo-olefins, e.g. 1-octene, 2-octene, cyclooctene.

2. Experimental

2.1. Catalysts preparation

2.1.1. The base support

The Mg/Al hydrotalcite (HT), the derived mixed oxide (CHT) and the reconstructed hydrotalcite structure via “memory effect” (RHT) were prepared according to procedures described in detail earlier [34–36].

The Mg/Al hydrotalcite with $Mg^{2+}/Al^{3+} = 3$ molar ratio was synthesized at constant pH = 10 by coprecipitation at low supersaturation using $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3 and NaOH. The resulting gel was aged under mild stirring at 70 °C during 18 h. The HT was then separated by filtration, washed with deionised water and dried at 90 °C during 24 h under nitrogen flow in order to avoid further contamination of the sample with atmospheric CO_2 .

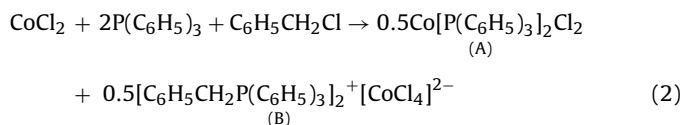
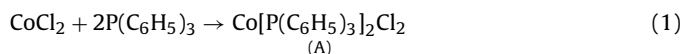
The CHT mixed oxide derived from HT was obtained by calcination of the dried HT at 400 °C during 18 h under nitrogen flow.

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.

2.1.2. The cobalt complex precursors

Co(II) phthalocyanine-tetrasulfonic acid tetrasodium salt was purchased from Fluka.

The bis-triphenylphosphine-dichlorocobalt (II) $Co[P(C_6H_5)_3]_2Cl_2$ (A) and an admixture of $Co[P(C_6H_5)_3]_2Cl_2$ and benzyltriphenyl phosphonium-tetrachlorocobaltate $[C_6H_5CH_2P(C_6H_5)_3]_2^+[CoCl_4]^{2-}$ (B) have been prepared according to the reactions:



Bis-triphenylphosphine-dichlorocobalt (II) $Co[P(C_6H_5)_3]_2Cl_2$ (A) was synthesized by mixing the hot alcoholic solutions of the reagents in the molar ratios described by Eq. (1) according to the method earlier described by Cotton et al. [37]. The alcohol used as solvent was absolute ethanol. The dark blue crystalline product obtained was washed several times with absolute ethanol and ethyl acetate then it was vacuum dried.

Reaction (2) was performed under nitrogen at 60 °C during 6 h using a mixture of 0.02 moles triphenylphosphine ($P(C_6H_5)_3$) with 0.01 moles benzylchloride $C_6H_5CH_2Cl$ and 0.01 moles $CoCl_2 \cdot 6H_2O$ solved in *n*-butanol. Then the solvent was evacuated under

vacuum. The precipitate displaying bright blue crystals was separated under nitrogen and recrystallized 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 $[C_6H_5CH_2P(C_6H_5)_3]^+[(C_6H_5)_3PCoCl_3]^-$ could not be obtained by this procedure [37].

2.1.3. The cobalt modified hydrotalcite-like catalysts

One cobalt modified hydrotalcite (CoMg/Al) 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 $CoCl_2 \cdot 6H_2O$ in order to correspond at $(Mg^{2+} + Co^{2+})/Al^{3+} = 3$ molar ratio and a concentration of 2% Co w/w (e.g. 3.5×10^{-4} mol Co g^{-1}) in the catalyst. However, the cobalt concentration as determined by AAS in the final catalyst was slightly lower than the desired value, e.g. 1.95% Co w/w (3.32×10^{-4} mol Co g^{-1}) probably due to the high value of the pH during the precipitation which did not allow the complete incorporation of cobalt in the hydrotalcite structure.

Three Co-containing hydrotalcite-like catalysts were obtained by impregnation of the parent HT with different Cobalt precursors: (i) $CoCl_2 \cdot 6H_2O$, (ii) $Co[P(C_6H_5)_3]_2Cl_2$ (A) and the admixture of $Co[P(C_6H_5)_3]_2Cl_2$ and $[C_6H_5CH_2P(C_6H_5)_3]_2^+[CoCl_4]^{2-}$ (A and B, respectively). The impregnation was performed by contacting the support, previously vacuum dried at 25 °C during 3 h, with acetone solutions of the cobalt precursors (Co concentration in acetone 6.5×10^{-3} mol L^{-1}) for 24 h at 25 °C. A strong and rapid adsorption of cobalt species took place, the blue acetone solutions became colorless and the solid supports turned to a blue-violet color. The resulting solids were filtered, washed three times with acetone, then with benzene and finally dried under vacuum (10^{-2} Torr) at 25 °C. The obtained catalysts were stored under nitrogen. Depending on the precursors these catalysts are further on mentioned as CoCl₂/HT, A/HT and AB/HT. The cobalt concentrations as determined by AAS were quasi identical for all three samples, 2.36% Co w/w (e.g. 4×10^{-4} mol g^{-1}) for CoCl₂/HT; and 2.15% Co w/w (e.g. 3.66×10^{-4} mol g^{-1}) for A/HT and AB/HT, respectively.

The above-mentioned procedure was also employed for the obtaining of AB complex supported on CHT and RHT, respectively. The resulting solids were named AB/CHT and AB/RHT. According to the results of AAS analysis, AB/CHT contains 2.23% Co w/w (3.79×10^{-4} mol g^{-1}) and has a violet-blue color similar to AB/HT, while AB/RHT contains only 1.93% Co w/w (3.28×10^{-4} mol g^{-1}) and has a brownish-green color.

Considering the similarity of the results obtained at AAS analysis which varied in the range 1.93–2.36% Co w/w, we may consider that all catalysts contained the same concentration of cobalt ca. 2% w/w.

2.2. Catalysts characterization

Chemical compositions were determined by AAS for the determination of the metal content as well as by EDX for the determination of Co, Mg, Al, Cl. Energy dispersive X-ray analysis (EDX) was performed with a SiLi detector from EDAX Inc. inside a scanning electron microscope model Inspect S from FEI.

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. In the diffracted beam a Ni filter, a curved graphite monochromator and a programmable divergence slit, enabling constant sampling area irradiation, were placed ($\lambda = 0.15418$ nm). Data were analysed using the PANalytical X'Pert HighScore Plus software package. The crystallites sizes were evaluated using the Scherrer formula.

The as-synthesized complexes and the cobalt modified hydrotalcites were characterized by DR-UV–vis–NIR in the range of 210–1500 nm. The spectra have been recorded with a Jasco V670

spectrometer equipped with an integration sphere. MgO was used as white reference.

DRIFTS (diffuse reflectance Fourier transformed infrared spectroscopy) spectra were recorded on a NICOLET 4700 spectrometer in the domain 400–4000 cm^{-1} . DRIFTS spectra averaged over 200 scans were refined by subtracting the spectrum of KBr used as background.

The specific surface area was estimated from the adsorption isotherm by the Brunauer–Emmett–Teller (BET) method and the corresponding pore size distribution using the Barrett–Joyner–Halenda (BJH) method from the N_2 adsorption–desorption isotherms. The N_2 -isotherms were collected on a Micromeritics ASAP 2020 apparatus after an in situ degassing procedure at 70 °C for 24 h.

2.3. Catalytic tests

The activity and selectivity of the catalysts were tested in the oxidation of cyclohexene with oxygen using isobutyraldehyde as reductant and acetonitrile as solvent. In a typical experiment 20 mg of catalyst were contacted with cyclohexene (0.04 mol) and isobutyraldehyde (0.08 mol) which were dissolved in 10 mL acetonitrile. All reagents were freshly distilled. Catalytic reactions were performed during 5 h at room temperature under 1 atm of O_2 in a sealed stirred flask (250 mL), provided with a manometer and an admission tube connected to an oxygen pressurized cylinder. Prior to the admission of the catalyst in the reaction mixture the reactor was purged with oxygen in order to remove the air from the system. During the experiment, the oxygen from the pressurized cylinder was introduced in the flask at the surface level of the reaction mixture in order to maintain the oxygen pressure at 1 atm as indicated by the manometer.

In the catalytic tests performed with other olefins, e.g. 1-octene, 2-octene and cyclooctene, the same number of moles (0.04 mol) as in the case of cyclohexene were added in the reaction mixture while maintaining all the other reaction conditions.

The reaction products were 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 standard samples (retention time in GC). The reaction products were identified also by mass spectrometer-coupled 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. The epoxide yield, the selectivity, the conversion of the olefin and the selectivity to by-products were evaluated. The turnover frequency for olefin transformation (TOF_O), the turnover frequency for

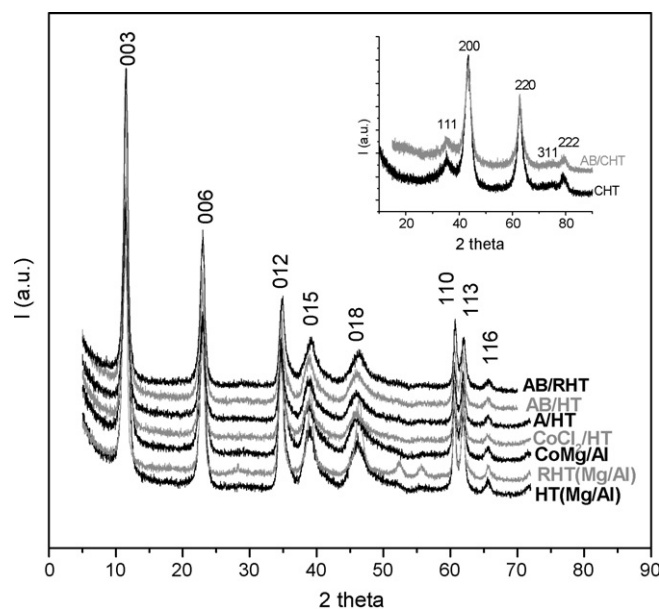


Fig. 1. XRD patterns of the supports and Co-containing catalysts.

epoxide formation (TOF_{EPO}) and the turnover number for epoxide formation (TON_{EPO}) were calculated using the formulae:

$$TOF_O = \frac{n_{O,i} - n_{O,tp}}{n_{Co} \cdot \tau} \quad [\text{moles}_{\text{olefin transformed}} \cdot \text{mol Co}^{-1} \cdot \text{h}^{-1}] \quad (3)$$

$$TOF_{EPO} = \frac{n_{EPO,tp}}{n_{Co} \cdot \tau} \quad [\text{moles}_{\text{epoxide formed}} \cdot \text{mol Co}^{-1} \cdot \text{h}^{-1}] \quad (4)$$

$$TON_{EPO} = \frac{n_{EPO,tp}}{n_{Co}} \quad [\text{moles}_{\text{epoxide formed}} \cdot \text{mol Co}^{-1}] \quad (5)$$

where $n_{O,i}$ is the number of moles introduced in the reaction mixture, $n_{O,tp}$ is the number of moles of olefin in the reaction mixture by the end of the reaction period, τ is the time in hours, n_{Co} is the number of moles of cobalt in the amount of catalyst utilized in the test, $n_{EPO,tp}$ is the number of moles of epoxide in the reaction product.

3. Results and discussion

3.1. Characterization of the catalysts by XRD analysis

The XRD patterns of the parents HT and reconstructed hydroxalcite RHT samples exhibit the typical pattern of a layered double hydroxide material (JCPDS file 70-2151, indexed in a hexagonal lattice with a $R3m$ rhombohedral symmetry, Fig. 1. XRD) while the

Table 1
Structural properties and the results of EDX analysis for the supports and cobalt containing catalyst samples.

Sample	XRD		EDX (at%)				EDX atomic ratio		
	Unit cell parameters		Mg	Al	Co	Cl	Mg/Al	Co/Al	Cl/Co
HT-structure	<i>a</i> (nm)	<i>c</i> (nm)							
HT (Mg/Al)	0.3056	2.3185	19.25	6.32	–	–	3.05	–	–
RHT	0.3055	2.3181	19.50	6.37	–	–	3.06	–	–
CoMg/Al	0.3056	2.3154	19.28	6.20	0.56	0.04	3.11	0.09	0.07
CoCl ₂ /HT	0.3056	2.3291	20.10	6.62	0.72	1.38	3.04	0.11	1.92
A/HT	0.3055	2.3209	19.20	6.29	0.65	1.15	3.05	0.10	1.78
AB/HT	0.3055	2.3232	19.22	6.37	0.64	1.78	3.02	0.10	2.78
AB/RHT	0.3050	2.3170	18.80	6.17	0.53	1.64	3.05	0.09	3.09
Mg(Al)O structure	<i>a</i> (nm)								
CHT	0.4181		27.04	8.82	–	–	3.07	–	–
AB/CHT	0.4180		24.85	8.10	0.54	1.27	3.08	0.07	2.35

Table 2
Textural properties of the parent supports and cobalt containing catalyst samples.

Samples	XRD analysis		Texture analysis	
	Crystallite sizes (nm)	BET surface area (m ² /g)	Pore size (nm)	Vol. ads. (cm ³ /g)
HT	9.1	131	18.9	0.6220
AB/HT	9.3	138	15.5	0.5351
CHT	3.2	250	14.4	0.8990
AB/CHT	4.2	229	15.0	0.8548
RHT	16.3	3	6.7	0.0054
AB/RHT	11.7	32	8.2	0.0647
CoCl ₂ /HT	9.3	113	21	0.5897
CoMg/Al	8.7	125	16.7	0.5562
A/HT	9.1	134	18.6	0.6130

pattern of the parent CHT support is that of a mixed oxide Mg(Al)O having MgO-periclase structure (JCPDS file 45-0946, indexed in a cubic symmetry inset from Fig. 1 XRD). The XRD patterns of the cobalt containing samples are similar to those of the Co-free samples with no extra peaks originating from crystalline cobalt species, indicating a high dispersion of cobalt on the supports. As it may be seen from the data presented in Table 1, no substantial modification of the *a* and *c* parameters were observed upon Co complexes incorporation on the HT and RHT supports which suggests that, more likely, the cobalt complexes covered preferentially the outer surface and in a very low amount the interlayer space, wherein they adopt more likely a flat-lying position. In the case of CoMg/Al the isomorphous substitution of Mg²⁺/Al³⁺ by Co²⁺/Co³⁺ is not to be 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 Co²⁺ and/or Co³⁺ with Mg²⁺ and/or Al³⁺. The XRD pattern of AB/CHT sample exhibits the same structure as the parent CHT with no extra peaks due to cobalt compounds.

The EDX analysis data regarding the Mg, Al, Co and Cl components are gathered in Table 2. A survey of results shows the preservation of the parent Mg/Al upon cobalt introduction. For the sample CoMg/Al prepared via coprecipitation the Mg/Al is close to the expected value 3 while the value of the Co amount introduced

in the structure is slightly lower than the one expected due to the synthesis conditions, namely the pH = 10 used. The traces of Cl still detected in this sample show that there are some cobalt species still outside the brucite type layer either in the interlayer space or on the external surface of crystallites while the main part of Co isomorphously substitutes Mg²⁺ or even Al³⁺ in the brucite-type layer. In the case of the sample AB/RHT, which incorporates also a slightly smaller amount of cobalt, this fact may be explained by the lower adsorption capacity of the RHT support as it may be seen from the data presented in Table 2. The main observation drawn from EDX analysis results is the correlation of the Cl/Co atomic ratios obtained for Co catalysts with the chemical formulae of the Co species used for the impregnation procedure. For CoCl₂/HT and A/HT samples obtained from CoCl₂·6H₂O and Co[P(C₆H₅)₃]₂Cl₂ respectively, the Cl/Co ratios are less or close to 2 while for samples prepared from an admixture of Co[P(C₆H₅)₃]₂Cl₂ and [C₆H₅CH₂P(C₆H₅)₃]₂⁺[CoCl₄]²⁻ (AB/HT, AB/RHT and AB/CHT) the Cl/Co atomic ratios exceed 2. The results suggest the existence of [CoCl₄]²⁻ in all the samples prepared from the admixture AB and in particular in the AB/RHT catalyst.

As it may be seen from the data presented in Table 2, there are no major differences in the pore structures of the samples containing AB complex deposited on HT, RHT or CHT compared to the corresponding parent hosts. One has to observe the low values of the surface areas of the reconstructed RHT and AB/RHT samples effect which has been already reported [29,36,38]. From this result one could assume that the accessibility of guest species in the interlayer space of the reconstructed layered structure is very poor and therefore we could consider that the complex Co species are deposited almost entirely on the external surface of the host RHT. The high surface areas of CHT and AB/CHT catalysts denote an open and accessible surface for both active catalytic species and reactants.

3.2. Characterization of the catalysts by DR-UV-vis-NIR analysis

The DR-UV-vis-NIR spectra of Cobalt containing catalysts as well as those of the neat complexes are presented in Fig. 2.

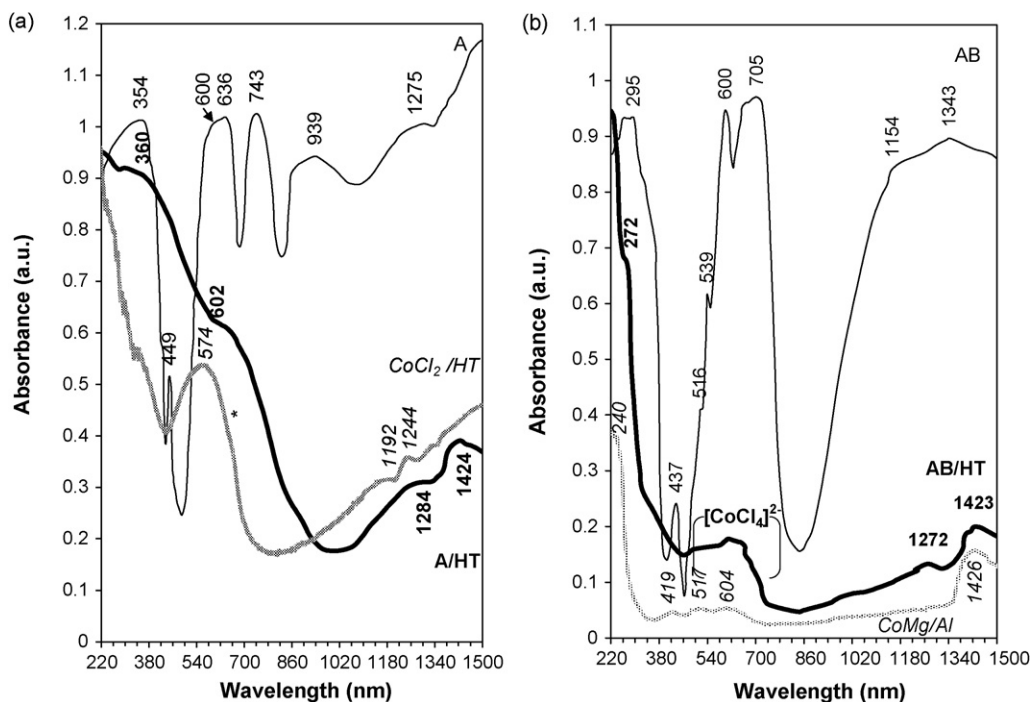


Fig. 2. DR-UV-vis-NIR spectra of the neat complexes and cobalt modified catalysts: (a) A, and catalysts A/HT and CoCl₂/HT; (b) AB complex and catalysts AB/HT, CoMg/Al.

The spectrum of CoCl_2/HT presented an intense and broad band at 574 nm characteristic for high spin hexacoordinated $\text{Co(II)} d^7$ species in CoCl_2 . A slight inflexion of this band at 625 nm (marked with an asterisk in Fig. 2a) suggests the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ species. There are also two other low intensity bands corresponding to hexacoordinated hydrated species $\text{Co(II)}(\text{H}_2\text{O})_4\text{Cl}_2$ at 1192 and 1244 nm [39]. The spectrum of CoMg/Al catalyst presented only the features characteristic for Co cation species in octahedral symmetry, consistent with the structure of the brucite-type layer [39,40]. The presence of the bands at 419 and 517 nm indicated that some of Co(II) ions were oxidized to Co(III) , while the bands at 604 (ν_2) and 1426 nm (ν_1) are characteristic for Co(II) in octahedral symmetry. This partial oxidation of Co(OH)_2 to Co(OH)_3 (or CoOOH) in basic media was also reported by Leroux and Zheng [40,41] who have showed that the oxidation is thermodynamically very favorable at low oxygen pressure which is reached during the aging period of the precipitate.

The spectra of A and AB complexes showed the characteristics specific for distorted tetrahedral symmetry of Co(II) species with very intense bands in the region of d–d transitions [37,39,42–44]. It was shown by Cotton et al. that the spectrum of complex anion is not related to the cation which was associated; the low symmetry components of the ligand field had no pronounced effect on the spectrum [37,42]. In the spectrum of AB, some of the bands corresponding to ligand to metal charge transition (LMCT) are overlapped by the bands characteristic to the benzyltriphenyl phosphonium cation around 300 nm [45]. The band for the d–d transition appears along with those corresponding to $\pi-\pi^*$, $n-\pi^*$ and (LMCT) transitions in $\text{P}(\text{C}_6\text{H}_5)_3$ [46,47].

The DR-UV–vis–NIR spectra of the catalysts prepared by the impregnation of the parent HT with acetonic solutions of A and AB complexes, revealed that upon impregnation the structures of both cobalt precursor complexes are altered, and the cobalt species are found mainly in octahedral symmetry. Thus, in the spectrum of A/HT the bands characteristic for Co(II) in octahedral coordination corresponding to dinuclear complex species $[\text{Mg}^{2+}[\text{Co}(\text{OH})_2\text{Cl}_2]^{2-}]$ formed upon the interaction of CoCl_2 released by complex A with $\text{Mg}(\text{OH})_2$ from the HT support are noticed at 602 (ν_2) and 1424 nm (ν_1). The presence of the broad band at 360 nm (ν_3) along with the large shoulder at 1284 nm (ν_1) indicate that there are also traces of Co(II) in tetrahedral symmetry. Neither the bands characteristic to hydrated Co(II) complex species nor those corresponding to Co(III) species were noticed.

In the spectrum of AB/HT, the presence of tetrahedral coordinated Co(II) anionic species $[\text{CoCl}_4]^{2-}$ is indicated by the large band with splittings in the region 600–700 nm and the band at 1272 nm (ν_1), while the band at 1423 nm indicates the presence of Co(II) species in octahedral symmetry similar to those noticed in the spectrum of A/HT. The intensity of the band corresponding to benzyltriphenyl phosphonium cation around 300 nm decreases dramatically compared to that in the unsupported complex AB.

3.3. Characterization of the catalysts by DRIFTS analysis

Due to the low amount of cobalt incorporated there were no major differences between the DRIFT spectra of the cobalt modified hydrotalcite-like catalysts when compared to the spectra of the parent support. This aspect may be seen from the DRIFTS spectra of AB/HT and HT presented as an example in Fig. 3.

The DRIFT spectra of AB complex showed the characteristic absorption bands of phosphine ligand (742–754; 692–705 cm^{-1}) along with the bands characteristic for monosubstituted benzene ring (706; 784; 926 cm^{-1}), the band for stretching vibration of C–H (ν_{CH}) in the range of 700–900 cm^{-1} (753; 784; 830 and 926 cm^{-1}), the band for ring vibration ($\nu_{\text{C=C}}$) in the range of 1450–1500 cm^{-1} and δ_{CH} in the range 950–1225 cm^{-1} (997; 1028 cm^{-1}).

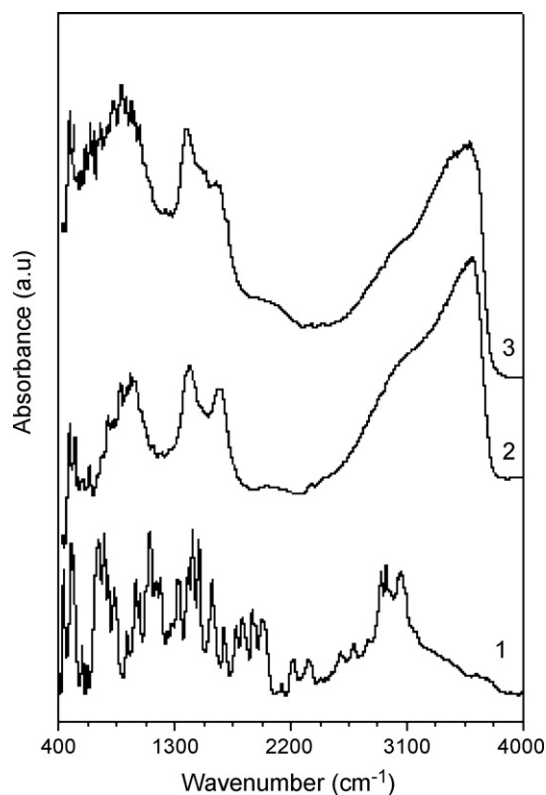


Fig. 3. DRIFT spectra of AB (1), HT (2) and AB/HT (3).

The parent HT presents the main absorption bands at 3500; 1600; 1390; 1358; 850–880 cm^{-1} .

In the spectrum of AB/HT the intense bands of the support overlapped the bands of the complex and there were only slight modifications of intensity for the bands of the support in the region 400–2200 cm^{-1} .

3.4. Catalytic tests results

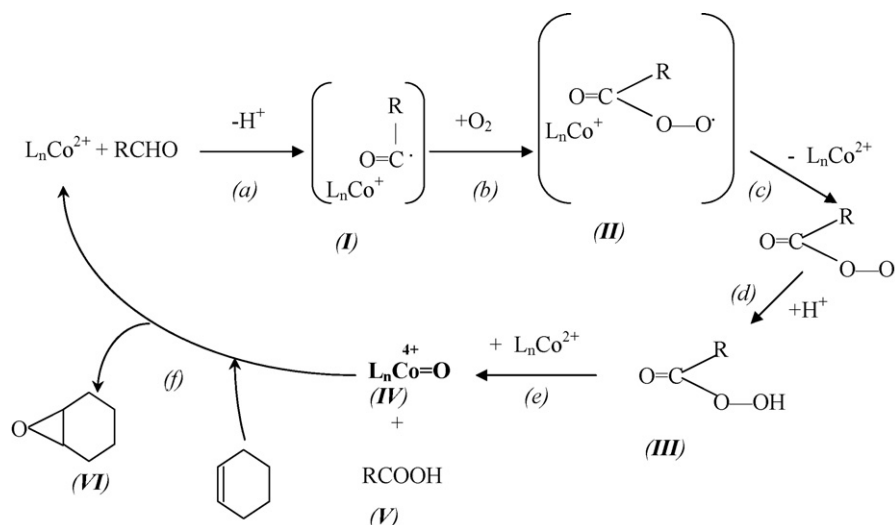
The activity and the selectivity of cobalt modified hydrotalcite-like catalysts prepared by different methods using different cobalt precursors have been evaluated for the oxidation of cyclohexene with molecular oxygen in the presence of isobutyraldehyde as reductant.

The reaction mechanism may be similar to the one proposed by Nam et al. [48] for the epoxidation of olefins by dioxygen in the presence of aldehydes when using cobalt (II) porphyrins or cobalt (II) cyclam complexes as catalysts which is illustrated by the reaction path indicated in Scheme 1.

The first step (a) represents the adsorption of the isobutyraldehyde (abbreviated as RCHO) on the cobalt complex species accompanied by the formation of intermediate complex species (I – an acyl radical adsorbed on L_nCo^+) following the release of a proton from the aldehyde and the reduction of Co^{2+} to Co^+ .

The second step (b), involves the undissociative adsorption of molecular oxygen on the intermediate complex species (I) with the generation of an intermediate complex species (II – an acylperoxy radical adsorbed on L_nCo^+).

In the third reaction step, (c), the L_nCo^{2+} species are regenerated following the release of the acylperoxy anion from the intermediate (II). The fourth reaction step (d) results in the formation of isobutyraldehyde-peroxyacid (III). In the fifth reaction step (e), the peroxyacid (III) acts as a strong oxidant towards L_nCo^{2+} species leading to the formation of an oxometallic active species (IV) playing a role



Scheme 1. The reaction mechanism for the oxidation of cyclohexene with molecular oxygen in the presence of isobutyraldehyde and Co-containing catalysts.

similar to the one played by hydrogen peroxide or alkylhydroperoxides in the oxidation mechanism proposed by Sheldon [3,4] and to the release of isobutyric acid (V) as a reaction by-product. In the final reaction step (f), the olefinic substrate (cyclohexene) interacts with the oxometallic active species (IV) generating the formation of the cyclohexane epoxide (VI) while regenerating the catalytic active species L_nCo^{2+} .

It was aimed to correlate the activity and selectivity of the catalysts with their structural and textural characteristics in order to find out in what extent they are affected by the location, the dispersion, the oxidation state and the coordination of cobalt cation as well as by the structure, and the porosity of the HT support.

The results obtained with a catalyst Co–Phtalocyanine $[(SO_3)_4]^-/HT$ (abbreviated as CoPht/HT) containing an amount of Cobalt equivalent to that of the other cobalt containing catalysts have been used as reference for the comparison. For this solid it has been found that the active phase, e.g. $[Co\text{-Phtalocyanine}(SO_3)_4]^{4-}$ is stable, located mainly in the interlayer region of the hydrotalcite

host and it is associated to the solid matrix through ionic bonds [18,43,44].

The preparation and the characterization of the cobalt modified HTs allowed several observations:

The catalyst $(CoMg)/Al = 3$ prepared by coprecipitation contains cobalt species mainly as $Co(OH)_2$ with pink color, rhombohedral brucite-type crystals. According to literature data hexacoordinated Co^{2+} ions substitute Mg^{2+} from the brucite-type layer [40,43].

In the case of impregnated catalysts A/HT and AB/HT in order to evaluate the stability of the cobalt complex species after their contact with the base support as well as the results of this interaction, the acetone phase separated at the end of the impregnation was analysed. It has been found that the amount of cobalt existing in the initial solution has been completely adsorbed by the support. The analysis of the solvent that was used for the washing of the solids revealed that neither cobalt nor chlorine were removed from the solid (Cobalt was under detection limit at AAS, and Cl could not be determined by the test reaction between the solvent

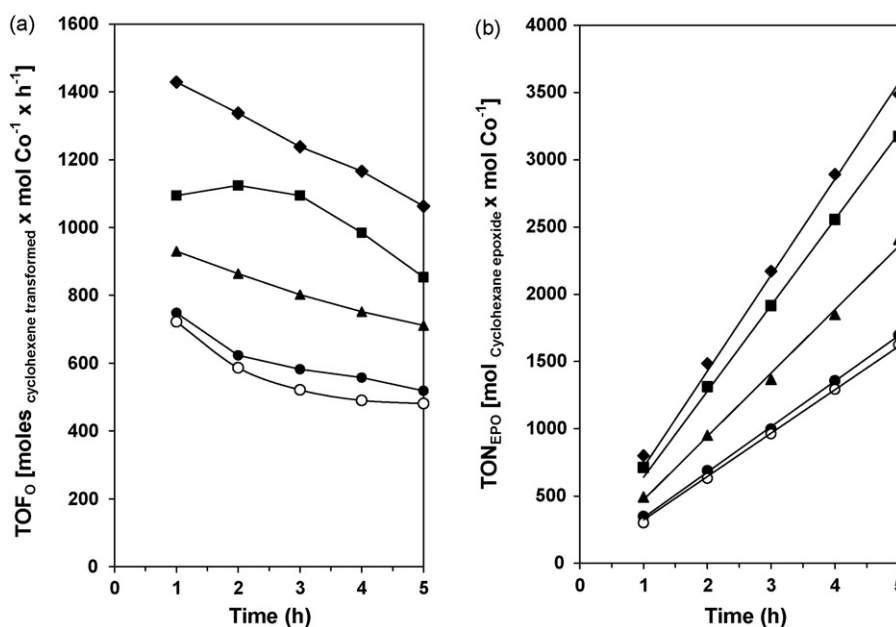


Fig. 4. The temporal variation of the turnover frequency for cyclohexene transformation TOF_0 (a) and the turnover number for cyclohexane epoxide formation TON_{EPO} (b) during the first 5 h of reaction time. Catalysts: (○) CoMg/Al; (●) CoCl₂/HT; (▲) A/HT; (■) AB/HT; (◆) CoPht/HT.

and AgNO_3 0.01 M). However, in the analysed liquid phases over about 90% of the phosphine contained in the complexes utilized for the impregnation has been recovered. This fact suggested that following the interaction with the base support, the initial complex (A or AB) is decomposed, the phosphine ligand is removed and the support acts as ligand in its place. In the case of CoCl_2/HT it has been noticed that cobalt was also entirely adsorbed on the support but there were traces of Mg and Al in the solvent used for the washing of the catalyst during the preparation, suggesting a partial dissolution of the support upon its contact with the solution of cobalt chloride that has a slightly acid pH. This fact may explain the higher concentration of cobalt as determined by AAS in this solid.

Among the investigated catalysts the most active were CoPht/HT and AB/HT which lead to cyclohexene conversions higher than 90% with epoxide yields ranging between 75% and 80% after 8 h reaction time. The activity and the selectivity of these solids have been also determined periodically in the first 5 h of the process when the yield to cyclohexane epoxide increases with a linear trend. The variation of the turnover frequency of cyclohexene TOF_O and the turnover number for cyclohexane epoxide formation TON_{EPO} are displayed in Fig. 4. It is noteworthy that in the case of CoPht/HT catalyst even if the values of TOF_O are higher than those obtained for AB/HT , they decrease linearly with the increase of the reaction time. Meanwhile for AB/HT catalyst a high value of TOF_O is maintained during the first 3 h of reaction. The catalysts A/HT , CoCl_2/HT and CoMg/Al had lower activities than AB/HT , but their temporal decrease of activity is less abrupt.

Depending on the cobalt precursor, both the catalytic activity and the production of epoxide increase in the following order: $\text{CoMg}/\text{Al} < \text{CoCl}_2/\text{HT} < \text{A}/\text{HT} < \text{AB}/\text{HT} < \text{CoPht}/\text{HT}$.

The results showed that excepting AB/HT the differences in selectivity among the cobalt modified catalysts are not significant compared to the reference material CoPht/HT . Thus, the selectivities for cyclohexane epoxide varied in the following order: CoCl_2/HT (65%) < CoPht/HT (66%) < $\text{CoMg}/\text{Al} = \text{A}/\text{HT}$ (69%) < AB/HT (74%).

The catalyst AB/HT obtained by impregnation of the parent HT with the admixture of complexes A and B, has an activity comparable to CoPht/HT . Its activity is due probably to a cooperative effect of CoCl_2 (formed by the decomposition of the complex A during the impregnation) and of the $[\text{CoCl}_4]^{2-}$ anion from complex B.

The difference of activity between CoCl_2/HT (obtained by impregnation of HT with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and A/HT (prepared by impregnation with $\text{Co}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2$) seems surprising taking into account the removal of the phosphine ligand from the complex A during the impregnation of the base support. However, as it was revealed by the results of DR-UV-vis analysis, the main difference between the complex species of CoCl_2/HT and A/HT catalysts consists in the fact that in the former the presence of hydrated complex species was noticed while in the case of the latter these hydrated species were absent probably because the initial complex A is not hydrated.

The better catalytic performances of AB/HT catalyst obtained by impregnation with the admixture of A and B complexes are due both to the cobalt anionic species $[\text{Co}(\text{OH})_2\text{Cl}_2]^{2-}$ generated following the interaction of CoCl_2 released by complex A with the support and to the complex anion species $[\text{CoCl}_4]^{2-}$ existing in the pre-formed complex B. These complex anion species may act also as compensation anions in the interlayer region of the HT.

Since AB/HT catalyst was the most active, the same cobalt precursors as those used for its preparation were utilized to impregnate two other supports having the same ratio Mg/Al (Mg/Al = 3), e.g. CHT the mixed oxide obtained by calcination of the parent HT, and the reconstructed hydrotalcite RHT which was obtained by rehydration of CHT. The results of the catalytic tests for cyclohexene epoxidation are displayed in Fig. 5.

AB/CHT is the most active catalyst for cyclohexane epoxide formation. Its better catalytic performances compared to AB/HT may be related to the higher surface area and to the more pronounced basicity of the carrier as it was showed in some of our previously reported results [49].

The catalytic activity of AB/RHT is situated between that of AB/HT and AB/CHT . The lower activity of AB/RHT compared to AB/CHT is a consequence of the lower surface area of the support.

In what concerns the higher activity of AB/RHT compared to AB/HT , this fact may be a consequence of the different morphology of the reconstructed hydrotalcite structure (RHT) obtained through “the memory effect” by the hydration of the calcined mixed oxides. In a previous paper we have showed that the rehydration of the calcined mixed oxides leads to hydrotalcite structures with smaller crystallites and more intense basicity than the parent structure due

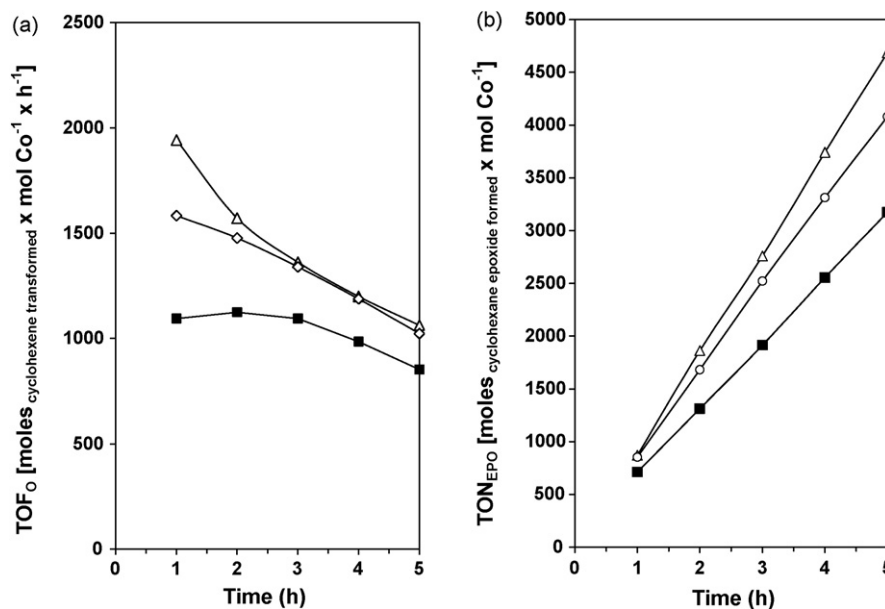


Fig. 5. Temporal variation of the turnover frequency for olefin transformation TOF_O (a) and the turnover number for epoxide formation TON_{EPO} (b) during the first 5 h of reaction time. Catalysts: (Δ) AB/CHT ; (\circ) AB/RHT ; (\blacksquare) AB/HT .

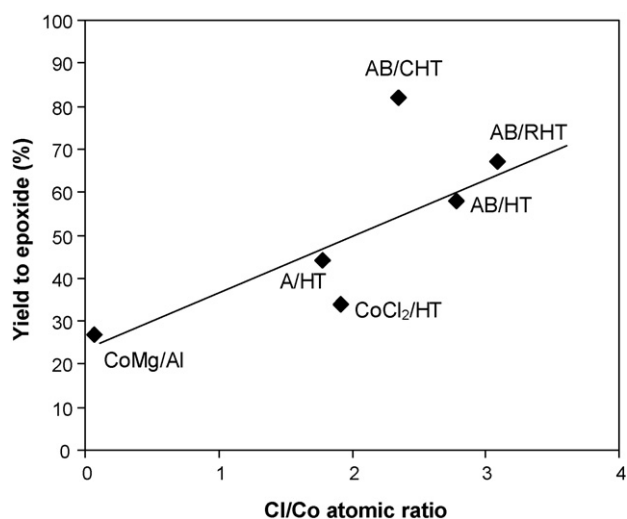


Fig. 6. Correlation between the chemical composition and the yield to cyclohexane epoxide for cobalt containing catalysts.

to the higher amount of OH^- anions in the interlayer and on the external surface of the solid [49].

The interaction of these OH^- groups with CoCl_2 (formed by the decomposition of the complex A during the impregnation) and the $[\text{CoCl}_4]^{2-}$ anion from complex B may lead to the oxidation of Co (II) to Co (III) yielding binuclear complex species which are similar to precursors of cobaltites.

Due to the morphologic peculiarities of the RHT the accumulation of cobalt catalytic active species is prevailing on the external surface of the carrier, and this fact favors the redox processes involved in the epoxidation of the hydrocarbon substrate.

A correlation between the results of EDX analysis and the catalytic activities of cobalt containing catalysts showed that for the hydrotalcite-like structures there is a linear variation of the yield to epoxide as a function of Cl/Co ratio in the solid as it may be seen from the results plotted in Fig. 6. The points corresponding to AB/CHT and CoCl_2/HT do not respect this trend probably because in the first case a different structure type of the support is involved, whereas in the case of the second there is a higher degree of hydration of the active cobalt complex species compared to the others.

As it may be seen from the results presented in Table 3, all Co-modified hydrotalcite-like catalysts presented selectivities to other oxidation products of cyclohexene besides cyclohexane epoxide in the range 12–35%, lower than the parent HT for which this selectivity reached 41%. The main effect induced by the modification with Co was the decrease of the amount of cyclohexenol obtained as by-product while allowing the formation of two other by-products: cyclohexane-1,2-dione and cyclohexane-1,2-diol. Both A/HT and CoCl_2/HT yielded the same distribution of by-products except for cyclohexenol. The lowest concentrations of by-products (12–26%) were obtained for the catalysts prepared by

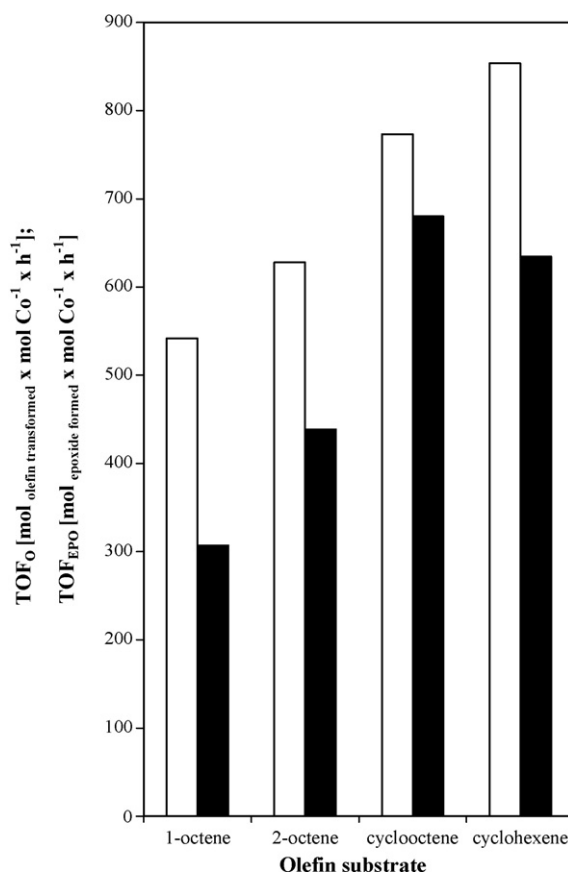


Fig. 7. The values of the turnover frequency for olefin transformation TOF_0 and turnover frequency for epoxide TOF_{EPO} for different olefin substrates after 5 h reaction time.

impregnation of the support with the admixture of cobalt complexes ($\text{Co}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2$, (A) and $[\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3]_2^+[\text{CoCl}_4]^{2-}$, (B), respectively). The selectivities for cyclohexane epoxide for AB/support catalysts varied between 74% and 88% after 5 h reaction time, indicating that for these catalysts the amount of by-products is rather low. The distribution of the by-products was also affected by the morphology, the surface area and the basicity of the support (e.g. HT, CHT, RHT).

The selectivity of AB/HT catalyst has been also investigated for different olefin substrates such as 1-octene, 2-octene and cyclooctene. The values of the turnover frequency for olefin transformation TOF_0 increase in the same order as the reactivity of the olefinic substrate 1-octene < 2-octene < cyclooctene < cyclohexene. The turnover frequency for epoxide TOF_{EPO} follows the same trend only in the series of C8 olefins. The lower value of TOF_{EPO} obtained in the case of cyclohexene transformation compared to the case of cyclooctene may be due to the higher reactivity of cyclohexene (Fig. 7).

Table 3

Distribution of the by-products (others than cyclohexane epoxide) obtained from cyclohexene following its oxidation on Co-modified hydrotalcite-like catalysts compared to the parent HT.

Catalyst	HT	CoMg/Al	CoCl_2/HT	A/HT	AB/HT	AB/RHT	AB/CHT
Oxidation product of cyclohexene							
Cyclohexenol	24	5	9	3.6	4.6	2.2	0.5
Cyclohexanone	1.7	0.8	0.8	0.4	0.6	1	0.8
Cyclohexenone	15.5	12.7	14.4	14.5	12.5	11.4	3.5
Cyclohexane, 1,2-dione	0	11.7	9.8	10.5	5.5	2.8	6.2
Cyclohexane, 1,2-diol	0	0.8	1	2	3	3	1
Total	41.2	31	35	31	26.2	20.4	12

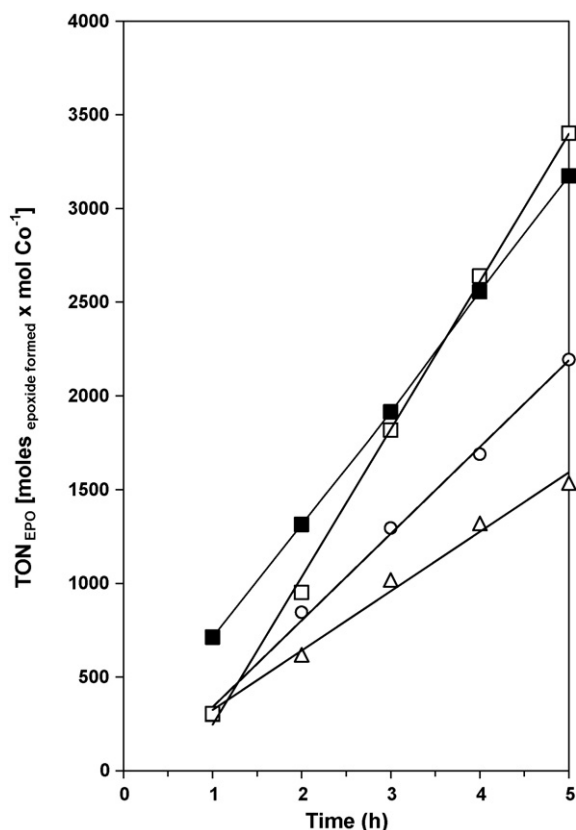


Fig. 8. Temporal variation of the turnover number for epoxide formation TON_{EPO} during the first 5 h of reaction time on AB/HT catalyst. Substrates: (Δ) 1-octene; (\circ) 2-octene; (\square) cyclooctene (\blacksquare) cyclohexene.

As it was the case for cyclohexene conversion, the values of the turnover number for epoxide formation increase linearly with the reaction time (Fig. 8), while their slopes are different as a consequence of the differences in the reactivities of the substrate.

4. Conclusions

The above presented results lead to the conclusion that the admixture of cobalt complexes bis-triphenylphosphine-dichlorocobalt (II) (A) and benzyltriphenyl phosphonium-tetrachlorocobaltate (B) may be used as cobalt precursor for the obtaining of new cobalt modified hydrotalcite-like catalysts containing $[CoCl_4]^{2-}$ active species which are active and selective for the oxidation of cyclohexene by molecular oxygen in the presence of isobutyraldehyde under mild and friendly conditions of temperature and pressure.

The higher performances of AB/HT catalyst are due to the dispersion and location of cobalt complex species in connection with the morphological and porous structure of the host support.

The hydrotalcite support seems to contribute to the stabilization of the cobalt active species and also plays a role in accelerating epoxidation by the construction of a reaction field based on the spatial interaction with guest molecules.

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