Heteronuclear iron(III)–chromium(III) hydroxo complexes and hydroxides, and their catalytic activity towards peroxidative oxidation of alkanes

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Abstract

The equilibrium compositions of the products of hydrolysis of Fe(III) and Cr(III) in their single or binary nitrate solutions, as a function of pH and neutralisation degree have been established and Fe(III)–Cr(III) hydroxides and products of their thermolysis have been obtained and characterized by potentiometric titration, thermal analysis, IR spectroscopy and X-ray powder diffraction, and an Fe(III)–Cr(III) interaction recognised in the binary systems. The obtained aquahydroxo complexes and metal hydroxides have been applied as catalysts for the homogeneous or heterogeneous, respectively, peroxidative oxidation of cyclohexane and cyclopentane to the corresponding ketones and alcohols, at room temperature. The effects of various parameters, such as pH, degree of neutralisation and reagents molar ratios, have been investigated and correlations between the catalytic activity and the form of the hydroxo complex were recognised for the homogeneous systems, whereas for the heterogeneous mixed (heteronuclear) hydroxides a synergic effect has been detected for the oxidation of cyclohexane, the catalytic activity (which can reach 30% yields and 30 turnover numbers (TONs)) being above those of the individual hydroxides.
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1. Introduction

The catalytic oxidation of hydrocarbons is a matter of current interest [1–12] and the selective oxygenation of cyclohexane, in particular, catalysed by μ-hydroxo diiron complexes [13], has been applied as a model reaction of such processes. Since peroxocomplexes are possible intermediates, chromium and iron peroxocomplexes have been studied extensively during the last decade [14–20] with the purpose of estab-

lishing the mechanisms of action of the metal ions in oxidation reactions of hydrocarbons, and also of designing biomimetic models of reactions catalysed by peroxidases or catalases [21,22]. These enzymes can contain an active center with two iron atoms joined by an oxide or hydroxide bridge [23,24], and the interaction of this {Fe$_2$(μ-O or μ-OH)} center with cyclohexane has been investigated [25–28].

Fe(III) and Cr(III) hydroxo- and oxo-complexes, hydroxides and oxides can show significant catalytic activity in reactions of hydrocarbon oxidation and hydroxylation [29–32]. For example, iron(III)-containing polytungstates [33] and peroxo adducts of iron(III)

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with N-ligands [34] can serve as inorganic and stable models of the Fe_2 active sites in methane monooxygenase. Barton studied the catalytic activity of iron and other 3d-metals solvocomplexes in the oxidation of cyclohexane by H_2O_2 [35], whereas the catalytic activity of solvocomplexes of Fe(III) in the hydroxylation of benzene by hydrogen peroxide was also investigated by others [36,37] who found that the activity and selectivity of the iron solvates are dependent on pH and therefore on the composition of the dissolved aqua-, hydroxo- and oxo-complexes. But in all these cases, the solvocomplexes that are responsible for the effective oxidation or hydroxylation of the substrate were not identified.

Electrochemical methods have also been successfully applied to the partial oxidation of alkanes and aromatics, namely involving electrogenerated in situ hydrogen peroxide in solutions containing a metal ion such as iron, copper or vanadium [6,38].

The oxidation of cyclohexane is an important process in organic synthesis in view of the broad usage of the products, cyclohexanone and adipic acid, in the production of ε-caprolactame and hexamethylene diamine which are the starting monomers for the synthesis of polyamide-6 and nylon-6,6. Salts of organic acids with metal ions of variable valence can be applied as industrial cyclohexane oxidation catalysts, and a catalytically active trinuclear μ-hydroxo-cobalt stearate was proposed [39]. Other catalytic systems using Fe, Mn and Co complexes are known [40–42] and an interesting aspect of the research is the attempt to find synergetic affects on the catalytic activity of mixtures [43–46], e.g. by including heterogeneous metals in the composition of the catalyst. However, the synergies in alkane oxidation reactions catalysed by mixed-metal (heteronuclear) hydroxo- and oxo-complexes have not yet been properly explored. Since our previous investigations [47] have shown that in several cases Fe(III) and Cr(III) may interact in solution to produce heteronuclear hydroxo complexes (HNHC), it has been proposed that such products could exhibit a non-additive catalytic activity [48], an hypothesis that we have addressed in the current study.

One of the most attractive ways for the catalyst preparation consists on the hydrolysis of metal ions followed by polycondensation, precipitation and thermal treatment of the obtained deposit (sol–gel technology) [49]. However, serious difficulties are encountered to correlate the process of formation of the polynuclear hydroxo complexes (PNHC) in water solutions and the composition, structure and thermal properties of the solid products synthesised on their basis, what hampers the establishment of the optimal conditions for the preparation of the catalysts and for their activity.

This work aims to contribute to overcome those problems, by studying the catalytic activity of dissolved aquahydroxo complexes of three-valent iron and chromium ions and the corresponding hydroxides and attempting to find a structure–activity relationship towards the oxidation of cyclohexane and cyclopentane by hydrogen peroxide in acetonitrile solutions. The Fe^{3+} and Cr^{3+} ions are selected on account of the following reasons: the easiness of change of the valence state and ability to exhibit either reduction or oxidation properties; their amphoteric properties; the ability to form hydroxoperoxo complexes and their sufficient stability [50–52]; the opportunity of occurrence of a synergistic effect upon formation of HNHC in solutions [53,54]; and the accessibility and low cost of the starting reagents [MCl_3, $M_2(SO_4)_3$, $M(NO_3)_3$ and NaOH] for the preparation of the catalysts. The choice of acetonitrile as a solvent is conditioned by its high co-ordination ability, high stability towards oxidation in the reaction conditions used (in contrast with other solvents, e.g. methanol, ethanol or acetone), by the similarity of boiling point with that of cyclohexane what allows and easy recirculation of the cyclohexane and solvent mixture, and also by the best results obtained in this solvent [55–58] for selected oxidation processes.

2. Experimental

2.1. Study of the Fe(III)–Cr(III) aquahydroxo complexes in water solutions

Dialysis of the aquahydroxo complexes of metals through a semipermeable cellophane membrane (which is permeable only to mononuclear complexes) after 7 days at 25 °C has been performed to find out the equilibrium composition of the hydrolysis products in the individual and binary Fe^{3+}–Cr^{3+} solutions. The metal nitrates have been used because NO_3^- ions practically do not influence the hydrolysis

of the cations. The total metal ion concentration in the working solution is 0.10 M, molar ratio $Fe^{3+}:Cr^{3+}$ = 1:1. For the preparation of this solution, 1 M $NaNO_3$ was added to the starting 1 M solution (2.5 ml) of metal nitrate in 1 M HNO_3 (the acid is necessary to prevent the spontaneous autohydrolysis of the metal ions in the initial solutions) to keep a constant value (0.5 M) of ionic strength, and a 2 M NaOH solution was added for a given degree of neutralisation, the final solution being then diluted with water up to 25 ml. A background solution was prepared by dilution of 1 M $NaNO_3$ to achieve that value of ionic strength.

The equilibrium pH values after the dialysis and the potentiometric titration of solutions (prepared similarly to experiments on dialysis) were measured at a constant temperature ($25 \pm 0.1\,^{\circ}$C) by using an Izmerpribor pH meter pH-150 with an ESL-15-11 glass electrode. The titration was conducted as follows: a 0.2 M NaOH solution was added from a burette (with the scale interval of 0.02 ml) to the starting solution of the metal nitrate (or mixture of metal nitrates) at a rate of 0.1 mol OH^-/(mol M^{3+} min).

2.2. Synthesis of the coprecipitated hydroxides and their analysis

0.1 M solutions of metal nitrates have been used for the preparation of the individual and coprecipitated hydroxides. The synthesis was performed by slow addition of a 0.2 M NaOH solution to the starting solution of metal nitrate (or mixture of solutions) during 30 min, with vigorous stirring, until the ratio $[OH^-]/[M^{3+}] = 3$. The obtained suspension was homogenised for 5 min and aged at 80 °C for 1 h, then filtered off, washed repeatedly with distilled water and alcohol until negative test of NO_3^- in the mother liquor. The obtained samples were dried in an oven at 25 °C up to constant weight. A sample was then dissolved in concentrated H_2SO_4 and analysed for the content of metal and nitrate ion. The iron(III) content was analysed by complexometric titration with sulfosalicylic acid at pH 2–3, whereupon in the same sample the chromium(III) content was determined by reverse titration by a nickel(II) nitrate solution in ammonia buffer with murexid as indicator. The content of nitrate ion was determined by direct potentiometry with an ion selective electrode.

The differential thermal analysis was conducted at a Paulik-Paulik-Erdey derivatograph with a heating rate of 10°/min. Samples of 0.500 g were heated from ambient temperature up to 1000 °C, and aluminium oxide was used as a standard. The IR spectra (KBr pellet) were measured on a SPECORD 75IR spectrophotometer in the range 4000–400 cm^{-1}. Diffractograms were obtained on a DRON-3 diffractometer, with Fe Kα rays and a Mn-filter, and the scan rate was 2°/min.

2.3. Catalytic activity of the hydroxocomplexes and hydroxides

The reaction mixtures were prepared as follows. In the case of homogeneous catalysis (dissolved hydroxocomplexes), to 1.00 ml of a 0.10 M solution with a certain $[OH^-]/[M^{3+}]$ concentration ratio (see above) were added 3.00 ml CH_3CN, 1.00 ml C_6H_{12} (cyclohexane) and 1.00 ml H_2O_2 (9.0 or 30%), in this order. The reaction mixture was stirred for 6 h at room temperature and normal pressure, then 0.20 ml of cyclopentanone (as internal standard) and 5.00 ml diethyl ether (to extract the substrate and the products from the reaction mixture) were added. The obtained mixture was stirred during 5 min and then a sample was taken from the organic phase and analysed by gas chromatography (GC) using a FISONS Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column (P/N 123-7032) and the JASCO-BORWIN v.1.50 software.

In the case of heterogeneous catalysts (individual and mixed hydroxides), the reagents were added in two different sequences: (i) 0.010–0.050 g of the metal hydroxide contained in the reaction flask were added 3.00 ml CH_3CN, 0–0.50 ml 65% HNO_3, 1.00 ml C_6H_{12} (cyclohexane) and 1.00 ml H_2O_2 (9.0 or 30%), in this order, and all the subsequent procedures are the same as in the above case of the homogeneous catalysts (the results obtained by this method are depicted in Table 7); (ii) 0.0125–0.05 mmol of the metal hydroxide contained in the reaction flask were added 3.00 ml CH_3CN, 10.00 mmol H_2O_2 (30%), 0–1.44 mmol 65% HNO_3 and 1.25–5.00 mmol C_6H_{12} (or 2.50–5.00 mmol C_5H_{10}), in this order, all the subsequent procedures being identical to those given above for the homogeneous catalysts, but 10.00 ml diethyl ether (instead of 5.00 ml) and cycloheptanone

(0.09 ml) as internal standard were used (the results obtained by this method are shown in Tables 5 and 6).

Blank experiments were performed for both cycloalkanes with H_2O_2, in the presence or in the absence of acid, and confirmed that no product of alkane oxidation was obtained unless the metal catalyst was used.

3. Results and discussion

3.1. Dissolved aquahydroxo complexes

The diagrams of distribution of the mono- and polynuclear aquahydroxo complexes as a function of the equilibrium pH (Figs. 1–3) and of $[OH^-]/[M^{3+}]$ (Table 1) were obtained by dialysis according to a reported [59] calculation procedure. The following values of the mononuclear hydrolysis constants were used in view of the experimental conditions (type of background electrolyte, ionic strength and temperature) [60]: $pK_1 = 2.3$ (Fe^{3+}) or 4.2 (Cr^{3+}), $pK_2 = 3.4$ (Fe^{3+}) or 5.5 (Cr^{3+}).

The diagram of distribution of the Fe(III) forms in the individual iron system (Fig. 1, Table 1) shows that this metal ion exists in solution entirely as the aqua ion $[Fe(H_2O)_6]^{3+}$ up to pH 0.9 (curve 1). Increasing

the pH results in the formation of the monohydroxo complex $[Fe(OH)(H_2O)_5]^{2+}$ (curve 2), at the expenses of the former up to a maximum ($\sim$16%) at pH 1.6 ($[OH^-]/[M^{3+}] = 0.0$) when the Fe(III) PNHC start to be formed (curve 3) reaching 100% at pH 2.3.

The distribution curves of the hydrolysis products in the individual Cr(III) system (Fig. 2) exhibit similar dependencies. Hence only the aquacomplex $[Cr(H_2O)_6]^{3+}$ is present up to pH 2.2 (curve 1), when the monohydroxo form (curve 2) starts to appear up to a maximum of 10% at pH 3.45 and $[OH^-]/[M^{3+}] = 2.0$. The Cr(III) PNHC (curve 3) are formed from pH 2.4 ($[OH^-]/[M^{3+}] \approx 0.25$) and the complete conversion of the mononuclear into the PNHC is observed at pH 4.2. It is noteworthy that the formation of dihydroxo complexes of iron and chromium does not take place, and therefore only the monohydroxo forms $[Fe(OH)(H_2O)_5]^{2+}$ and $[Cr(OH)(H_2O)_5]^{2+}$ play, in a broad pH range, a relevant role in the homopolynuclear hydrolysis of those metal ions [61,62].

By comparing the above mentioned diagrams with those for the binary Fe^{3+}–Cr^{3+} mixtures (Fig. 3), one observes non-additive hydrolytic behaviours of these metal ions. In fact, the hydrolysis of the Fe^{3+} and Cr^{3+} ions in the mixture starts at more acidic media (pH 0.75 and 1.6, respectively) in comparison with the individual solutions. Moreover, the formation
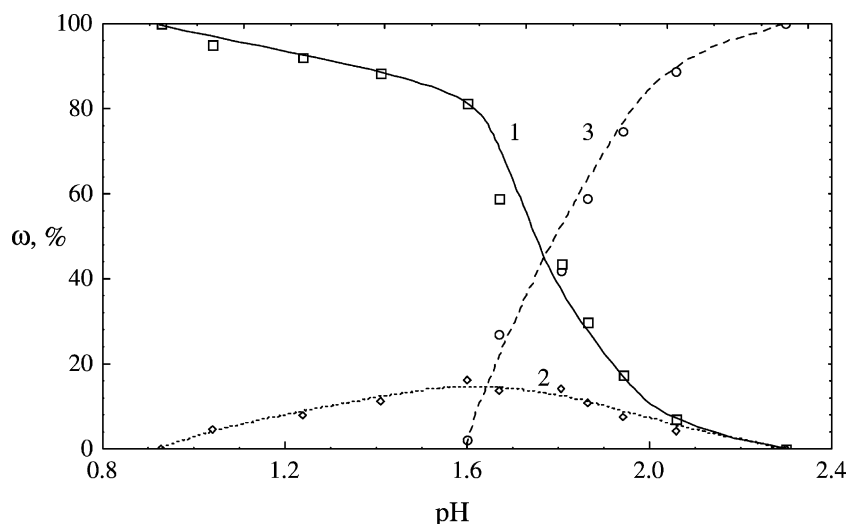

Fig. 1. Diagram of distribution of the aquahydroxo complexes as a function of pH for the Fe(III)–$NO_3{}^-$–H_2O system: (1) $[Fe(H_2O)_6]^{3+}$; (2) $[Fe(OH)(H_2O)_5]^{2+}$; (3) PNHC Fe(III).
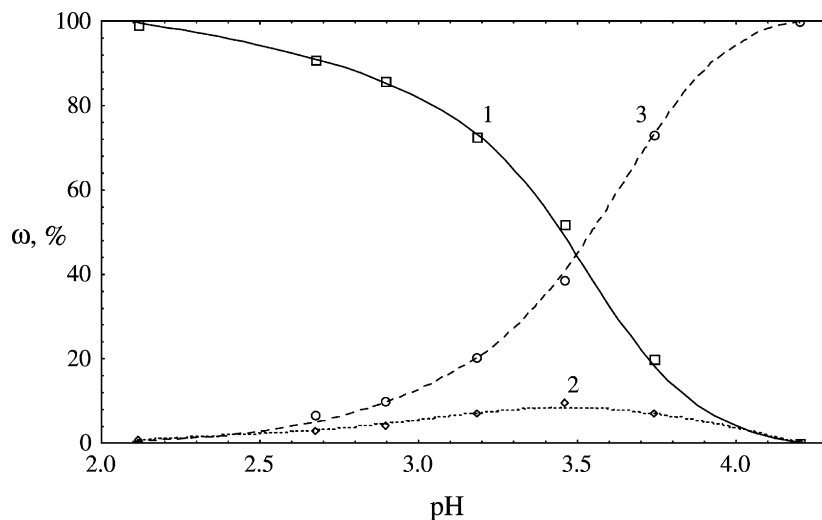
Fig. 2. Diagram of distribution of the aquahydroxo complexes as a function of pH for the Cr(III)–NO$_3{}^-$–H$_2$O system: (1) [Cr(H$_2$O)$_6$]$^{3+}$; (2) [Cr(OH)(H$_2$O)$_5$]$^{2+}$; (3) PNHC Cr(III).

of the Fe(III) and Cr(III) polymeric particles in the binary mixture also initiates at more acidic media (e.g. by 0.8 pH in the later) than the individual systems. These observations indicate that the Fe(III) and Cr(III) aquacomplexes interact with formation of HNHC.

A general scheme for the heteropolynuclear hydrolysis in the binary mixture can be presented as follows. Starting at pH 1.6 ([OH$^-$]/[M^{3+}] = 0.0), [Cr(H$_2$O)$_6$]$^{3+}$ interacts with the monohydroxo complex [Fe(OH)(H$_2$O)$_5$]$^{2+}$ with formation of
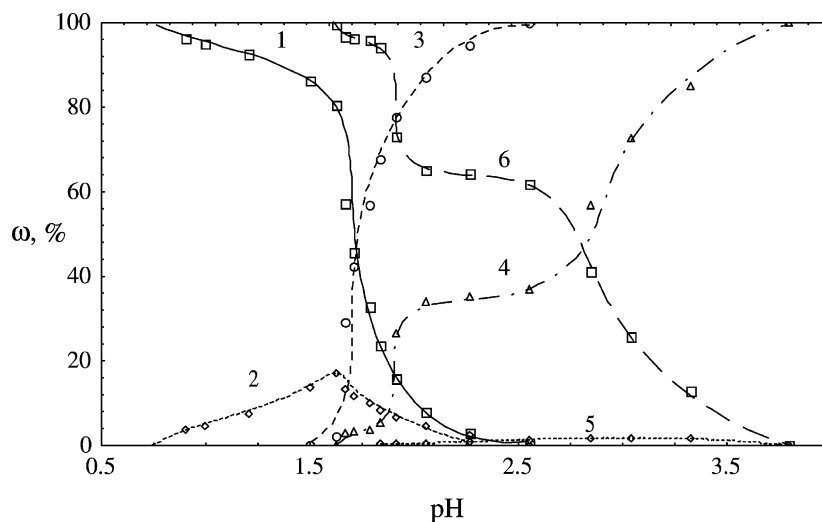

Fig. 3. Diagram of distribution of the aquahydroxo complexes as a function of pH for the Fe(III)–Cr(III)–NO$_3{}^-$–H$_2$O system: (1) [Fe(H$_2$O)$_6$]$^{3+}$; (2) [Fe(OH)(H$_2$O)$_5$]$^{2+}$; (3) PNHC Fe(III); (4) [Cr(H$_2$O)$_6$]$^{3+}$; (5) [Cr(OH)(H$_2$O)$_5$]$^{2+}$; (6) PNHC Cr(III).

Table 1
Distribution of the aquahydroxo complexes (ω, %) as a function of the neutralisation degree of the solution

$[OH^-]/[M^{3+}]$	0.00	0.50	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00
Fe^{3+}–NO_3^-–H_2O (ω, %)															
$[Fe(H_2O)_6]^{3+}$	91.9	88.5	81.5	–	58.9	–	43.6	–	29.8	–	17.6	–	6.9	–	0.0
$[Fe(OH)(H_2O)_5]^{2+}$	8.1	11.5	16.5	–	13.8	–	14.0	–	10.9	–	7.7	–	4.0	–	0.0
PNHC Fe(III)	0.0	0.0	2.0	–	27.3	–	42.4	–	59.3	–	74.7	–	89.1	–	100.0
Cr^{3+}–NO_3^-–H_2O (ω, %)															
$[Cr(H_2O)_6]^{3+}$	99.9	99.8	99.2	–	90.8	–	85.7	–	72.5	–	52.0	–	20.0	–	0.0
$[Cr(OH)(H_2O)_5]^{2+}$	0.1	0.2	0.8	–	2.7	–	4.3	–	7.0	–	9.5	–	6.9	–	0.0
PNHC Cr(III)	0.0	0.0	0.0	–	6.5	–	10.0	–	20.5	–	38.5	–	73.1	–	100.0
Fe^{3+}–Cr^{3+}–NO_3^-–H_2O (ω, %)															
$[Fe(H_2O)_6]^{3+}$	92.4	86.2	80.5	57.5	45.8	32.8	23.9	15.8	8.0	2.7	0.0	0.0	0.0	0.0	0.0
$[Fe(OH)(H_2O)_5]^{2+}$	7.6	13.8	17.2	13.6	11.8	10.3	8.5	6.5	4.5	2.5	0.0	0.0	0.0	0.0	0.0
PNHC Fe(III)	0.0	0.0	2.3	28.9	42.4	56.9	67.6	77.7	87.3	94.8	100.0	100.0	100.0	100.0	100.0
$[Cr(H_2O)_6]^{3+}$	99.9	99.8	99.7	99.6	96.3	96.0	94.3	73.0	65.3	64.1	61.6	41.3	25.8	13.0	0.0
$[Cr(OH)(H_2O)_5]^{2+}$	0.1	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.8	1.4	1.8	1.8	1.8	0.0
PNHC Cr(III)	0.0	0.0	0.0	3.1	3.4	3.6	5.3	26.6	34.2	35.1	37.0	56.9	72.4	85.2	100.0

heteronuclear Fe(III)–Cr(III) hydroxo complexes such as that shown in reaction (1):

$$(1)$$
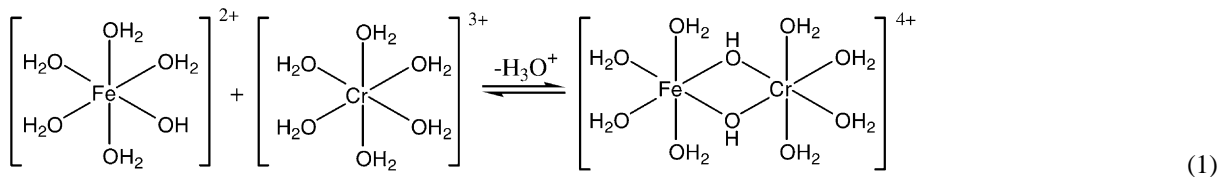
This is suggested by the identical pH values for the beginning of the formation of the polynuclear Cr(III) and Fe(III) hydroxo polymers. The distribution curves of the aqua and polynuclear Cr(III) forms (Fig. 3, curves 4 and 6) testify the occurrence of two sequential processes. The first one is the formation of the Fe(III)–Cr(III) HNHC up to pH 2.55 ($[OH^-]/[M^{3+}] =$ 0.0) at the expenses of about 40% of $[Cr(H_2O)_6]^{3+}$. The monohydroxo species $[Cr(OH)(H_2O)_5]^{2+}$ is formed upon increasing the addition of base (curve 5), but its amount is always insignificant due to its transfer into homopolynuclear Cr(III) particles.

The potentiometric titration curves of the Fe^{3+} and Cr^{3+} solutions and their mixture, by a NaOH solution, are depicted in Fig. 4. The titration of the individual solutions (curves 1 and 2) shows two equivalence points at $[OH^-]/[M^{3+}]$ ca. 1 and ca. 4. The first one corresponds to the neutralisation of $[M(H_2O)_6]^{3+}$ with formation of the corresponding monohydroxo complexes and the second one to the precipitation of the metal ions as PNHC. The plateau in the $[OH^-]/[M^{3+}]$ range of 0.5–2.5 (curve 1) and 1.0–2.5 (curve 2) corresponds to the hydrolysis of polynuclear Fe(III) and Cr(III) species [53]. The pH value of the middle of such a plateau corresponds to the overall constant of the polynuclear hydrolysis [63], i.e. $pK_{Fe(III)} = 2.45$, $pK_{Cr(III)} = 5.27$.

Three pH jumps are observed in the titration curve of the mixture of the iron(III) and chromium(III) solutions (curve 3). Apparently, the first one is connected to the neutralisation of $[M(H_2O)_6]^{3+}$ (M = Fe, Cr) with formation of the corresponding monohydroxo complexes $[M(OH)(H_2O)_5]^{2+}$. The second one, relevant to the predominant precipitation of the polynuclear Fe(III) particles, starts at $[OH^-]/[M^{3+}] = 2.3$ and pH 2.8, whereas the third one, with equivalence point at pH 8.0 ($[OH^-]/[M^{3+}] = 4.0$), corresponds to the complete precipitation of polynuclear Cr(III) species. Qualitative comparison of the titration curve of the binary solution (curve 3) with the hypothetical additive one (curve 4 as the semi-sum of curves 1 and 2) and the curves for the individual solutions indicates
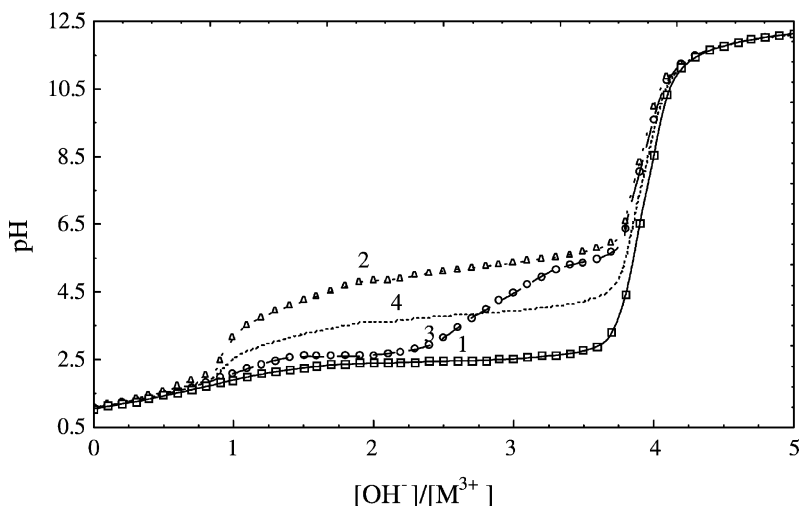
Fig. 4. Potentiometric titration curves of the metal nitrates in water solution: (1) Fe(III); (2) Cr(III); (3) Fe(III)–Cr(III); (4) Fe(III) + Cr(III) [hypothetical additive curve $(1 + 2)/2$].

the change of the individual hydrolytic behaviours of the Fe^{3+} and Cr^{3+} ions when they are both present.

3.2. Hydroxides and products of their thermolysis

The obtained hydroxides were subject to differential thermal analysis for clearing up the phase transfer ranges and for direct definition of the water content (Fig. 5). The mass loss (TG) has been recalculated in mol H_2O/mol product (M_2O_3), what allows to analyse the obtained thermogravimetric curves of the hydrox-

ides decomposition under a stoichiometric point of view. One endo and two exo effects are observed in the DTA curve of the 100% Fe(III) sample (Fig. 5a) at the 80–225, 225–300 and 495–645 °C temperature ranges, respectively. The first endo effect corresponds to the dehydration of amorphous hydroxide with loss, per mol M_2O_3 product, of 3.44 mol co-ordinated water and decomposed OH-groups from the near-surface layer, which is ligated by bonds with the greater ionic character (Table 2). The exo effect with maximum at 260 °C reflects the partial crystallisation of amorphous

Table 2
Results of thermogravimetric and chemical analyses of the obtained hydroxides

	Composition		
	100% Fe(III)	100% Cr(III)	50% Fe(III)–50% Cr(III)
Temperature of the thermal effect (°C)[a]			
I	80–225 (130)	60–210 (140)	80–270 (150)
II	225–300 (260)	210–365 (230)	–
III	495–645 (560)	365–415 (385)	450–560 (500)
Mass loss (mass%)[b]			
I	27.0 (3.44)	30.0 (4.90)	37.6 (11.16)
II	1.4 (0.18)	12.5 (1.99)	–
III	–	5.8 (1.00)	1.1 (0.38)
Σ	30.2	48.3	41.6
Mole ratio Fe_2O_3:Cr_2O_3:H_2O	1:0:3.84	0:1:7.89	1:1:12.35

[a] Temperature of the maximum is given in parentheses.
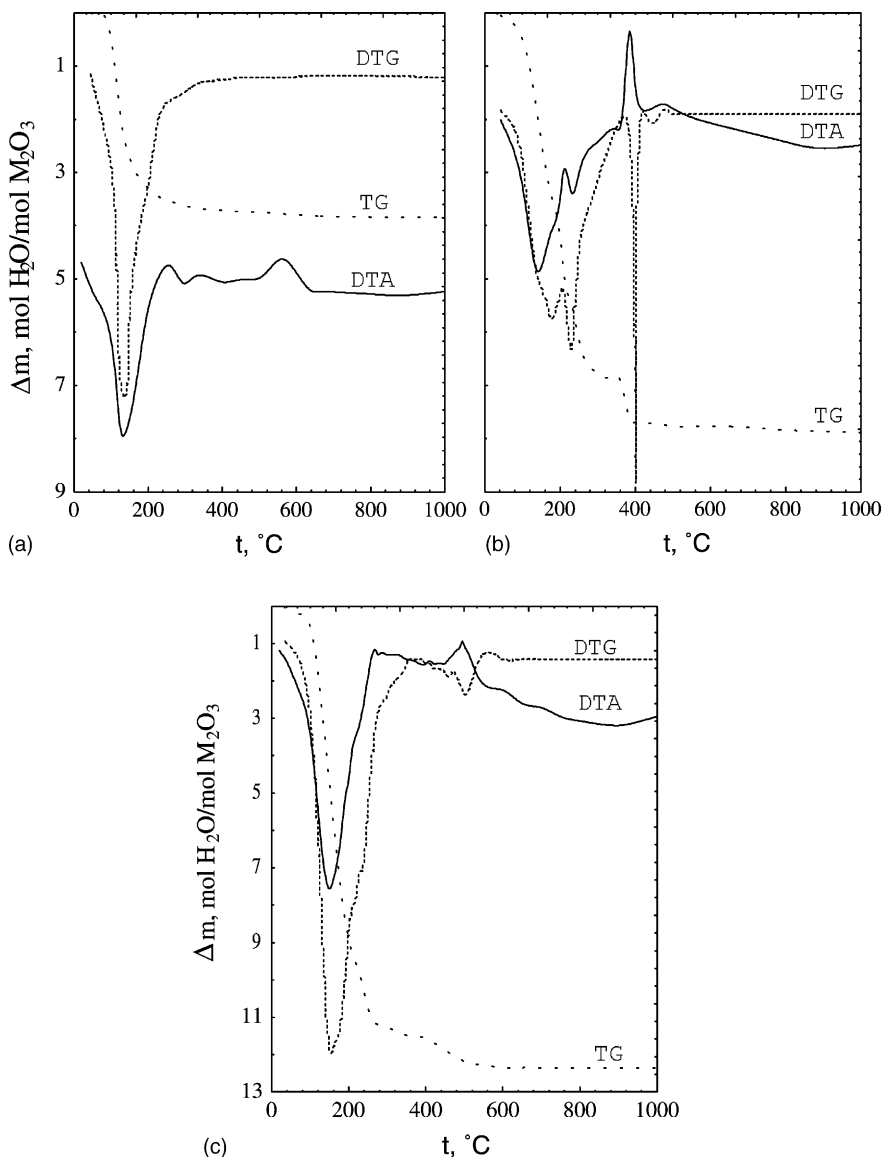[b] mol H_2O/mol M_2O_3 is given in parentheses.

Fig. 5. Results of the thermogravimetric analysis of hydroxides: (a) Fe(III); (b) Cr(III); (c) Fe(III)–Cr(III).

hydrate γ-$Fe_2O_3 \cdot nH_2O$ with simultaneous loss of a minor quantity of water. Further heating of the sample results in its complete dehydration and the broad exo effect with maximum at $560\,^\circ$C corresponds to the phase transfer of γ-Fe_2O_3 to α-Fe_2O_3 (hematite, ICDD file 13-534), what is confirmed by results of the X-ray powder diffraction of the final product of thermolysis (Table 3).

Two endo and one exo effects are observed in the DTA curve of the chromium(III) hydroxide at the temperature ranges of 60–210, 210–275 and 365–415 $^\circ$C, respectively (Fig. 5b). The endoeffect with maximum at 140 $^\circ$C corresponds to the loss of ca. 5 mol water/mol M_2O_3 (Table 2). The presence of the bend at 190 $^\circ$C confirms a composite character of the dehydration conditioned in particular by the existence of

Table 3
Basic results of the X-ray powder phase analysis of the products of the Fe(III), Cr(III) and Fe(III)–Cr(III) hydroxides decomposition until 1000 °C

d_{exp} (Å)	$(I/I_0)_{exp}$ (%)	d_{ref} (Å)	$(I/I_0)_{ref}$ (%)	Phase
Fe(III)				
3.671	46	3.66	25	Hematite-α-Fe_2O_3
2.697	99	2.69	100	Hematite-α-Fe_2O_3
2.521	100	2.51	50	Hematite-α-Fe_2O_3
2.206	40	2.201	30	Hematite-α-Fe_2O_3
1.838	40	1.838	40	Hematite-α-Fe_2O_3
1.690	60	1.695	65	Hematite-α-Fe_2O_3
1.598	14	1.596	16	Hematite-α-Fe_2O_3
1.485	41	1.484	35	Hematite-α-Fe_2O_3
1.453	45	1.452	35	Hematite-α-Fe_2O_3
1.310	20	1.310	20	Hematite-α-Fe_2O_3
Cr(III)				
3.625	62	3.633	74	Hexagonal-Cr_2O_3
2.655	100	2.660	100	Hexagonal-Cr_2O_3
2.474	94	2.480	96	Hexagonal-Cr_2O_3
2.175	48	2.176	38	Hexagonal-Cr_2O_3
1.815	43	1.816	39	Hexagonal-Cr_2O_3
1.670	83	1.672	90	Hexagonal-Cr_2O_3
1.462	37	1.465	25	Hexagonal-Cr_2O_3
1.430	44	1.431	40	Hexagonal-Cr_2O_3
Fe(III)–Cr(III)[a]				
3.668	48	3.68	80	Hexagonal-$(FeCr)_2O_3$
2.679	100	2.69	80	Hexagonal-$(FeCr)_2O_3$
2.505	71	2.51	80	Hexagonal-$(FeCr)_2O_3$
2.186	33	2.19	80	Hexagonal-$(FeCr)_2O_3$
1.828	38	1.83	80	Hexagonal-$(FeCr)_2O_3$
1.680	61	1.68	100	Hexagonal-$(FeCr)_2O_3$
1.479	29	1.47	80	Hexagonal-$(FeCr)_2O_3$
1.442	27	1.44	90	Hexagonal-$(FeCr)_2O_3$
1.301	21	1.30	90	Hexagonal-$(FeCr)_2O_3$

[a] Homogeneous solid solution.

different types of co-ordinated water [64]. The second endoeffect starts at the temperature of 210 °C with a maximal velocity of decomposition at 230 °C and reflects the loss of 2 mol water, what corresponds to the decomposition of 4 mol terminal OH-groups in the starting hydroxide, e.g. according to the reaction $Cr_2(OH)_6 \rightarrow Cr_2O_2(OH)_2 + 2H_2O$. The exo effect with maximum at 385 °C corresponds to the process of self-heating and transfer of substance from the amorphous into a crystalline state, with emission of 1 mol bound H_2O/mol M_2O_3, what is equivalent to the decomposition of 2 mol OH-groups. The final product of thermolysis according to X-ray powder diffraction (Table 4) is Cr_2O_3 (ICDD file 6-0504).

The thermolysis of the coprecipitated Fe(III)–Cr(III) hydroxides (Fig. 5c) is more complicated than those of individual hydroxides. The major endoeffect is observed at the temperature range 80–270 °C with the maximum at 150 °C and results from the removal of all the co-ordinated H_2O and majority of OH-groups. There is only a twist at 220 °C instead of the second thermal effect observed with the samples of the individual hydroxides. Heating the sample to temperatures above 270 °C promotes further dehydration and the last portions of water are removed at 500 °C. The maximum crystallisation rate corresponds to this temperature. The non-additivity in thermal properties of individual and coprecipitated hydroxides, expressed in temperature ranges, amount of removed water and crystallisation temperature, evidences an interaction between iron(III) and chromium(III) upon co-precipitation with formation of an individual compound of variable composition, rather then of a mechanical mixture of hydroxides. This is confirmed by X-ray powder diffraction (Table 3) which indicates that the product of the complete thermolysis of the coprecipitated Fe(III)–Cr(III) hydroxides represents a homogeneous solid solution (ICDD file 2-1357).

The obtained hydroxides and products of their thermolysis were studied by IR spectroscopy with the purpose of defining some features of the interaction of the metal ions and of the character of the bonds of water. The spectra of hydroxides (Fig. 6, spectra 1–3) in the 3600–3000 cm^{-1} range contain broad bands assigned to stretching vibrations of H_2O molecules and OH-groups bound by hydrogen bridges, in accord with the polymeric character of the hydroxides. The deformation vibrations of the OH bonds in water are exhibited in the range 1635–1630 cm^{-1}, whereas the oscillating vibrations of water appear at 850–840 cm^{-1}. In addition, the co-ordinated water absorbs in the low-frequency 600–300 cm^{-1} range (rotating vibrations of the molecule as a whole) [65]. The bands at 1480–1350 cm^{-1} cannot be clearly assigned and can be due to vibrations of OH-groups bound by hydrogen bridges, to water molecules or impurity ions. The analysis of the content of nitrate ions has shown that it is present only in minor quantities (<0.5 mass%) and therefore we may eliminate their contribution to the IR spectra. The lines with a maximum absorption at the 1020–1075 and 500–700 cm^{-1} ranges belong to the vibrations of hydroxobridges

Table 4

Catalytic activity of the Fe(III), Cr(III) and Fe(III)–Cr(III) aquahydroxo complexes towards peroxidative oxidation of cyclohexane by hydrogen peroxide (homogeneous systems)[a]

$[OH^-]/[M^{3+}]$	pH	Cyclohexanol		Cyclohexanone		Total yield[b]	Molar ratio ketone:alcohol
		Yield[c]	TON[d]	Yield[c]	TON[d]		
Fe(III)							
0.0	1.40	0.16	0.15	5.21	4.85	5.38	32:1
1.0	2.05	1.65	1.54	4.38	4.10	6.03	2.6:1
2.0	2.30	0.86	0.78	2.53	2.33	3.38	2.9:1
3.0	2.35	0.54	0.49	1.74	1.61	2.27	3.2:1
4.0[e]	7.17	0.01	0.05	0.82	0.76	0.83	137:1
Cr(III)							
0.0	1.06	0.00	0.00	0.04	0.01	0.05	_[f]
1.0	2.12	0.00	0.00	0.01	0.01	0.01	_[f]
2.0	3.75	0.01	0.00	0.44	0.42	0.45	44:1
3.0	4.25	0.12	0.11	1.06	1.25	1.18	8.8:1
4.0[e]	11.30	0.44	0.42	1.79	1.63	2.23	4.1:1
Fe(III)–Cr(III)							
0.0	1.35	0.75	0.69	2.34	2.13	3.09	3.1:1
1.0	2.20	0.86	0.78	2.77	2.46	3.62	3.2:1
2.0	2.40	0.50	0.46	1.98	1.85	2.48	3.9:1
3.0	3.15	0.48	0.43	1.89	1.80	2.38	4.0:1
4.0[e]	8.45	0.02	0.02	0.26	0.21	0.26	12:1

[a] $n(C_6H_{12}):n(H_2O_2):n(M^{3+}) = 92.6:88.2:1.0$; for other experimental conditions, see the Section 2.

[b] Cyclohexanol + cyclohexanone.

[c] Mol product/100 mol cyclohexane. Values lower than 0.005 are not given.

[d] Mol product/mol catalyst. Values lower than 0.005 are not given.

[e] A precipitate formed in the basic medium.
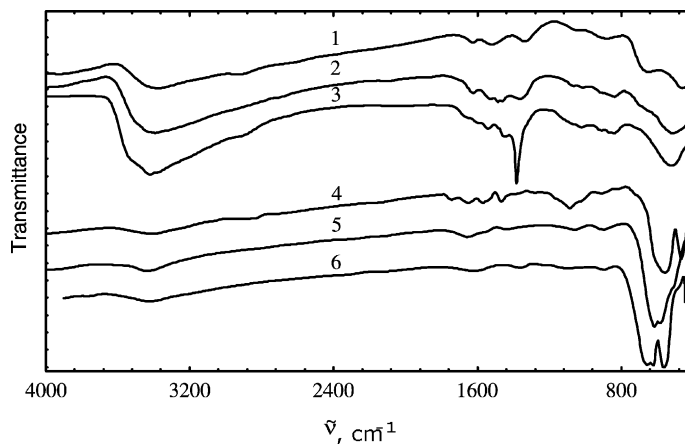
[f] Accurate value unavailable.

Fig. 6. IR spectra of hydroxides (1–3) and products of their thermolysis (4–6): (1 and 4) Fe(III); (2 and 5) Fe(III)–Cr(III); (3 and 6) Cr(III).

bonds M(μ-OH)$_2$M and stretching vibrations of M–O bonds. The shift and splitting of some characteristic bands in the spectrum of the coprecipitated hydroxides (Fig. 6, spectrum 2) in comparison with those of the individual hydroxides (spectra 1 and 3) reflect a change in the force constants, possibly resulting from a mutual influence of the iron(III) and chromium(III) centres. This can be accounted for by the formation of an Fe(III)–Cr(III) heteronuclear hydroxide.

The spectral pattern of the products of thermolysis has a simpler appearance (spectra 4–6) due to the vibrations of only strictly particular groups of atoms. Concerning the stretching, deformation and pendular vibrations of water, the weak bands corresponding to the vibration of moisture adsorbed from air are observed. Different types of vibrations of oxobridges M(μ-O)$_2$M appear at 1100–700 cm^{-1}. The occurrence of an absorption at 1060 cm^{-1} in the spectrum 5 of the products of thermolysis of coprecipitated hydroxides, instead of that at 1092 cm^{-1} characteristic for a 100% Fe(III) sample (spectrum 4), can be connected with the presence of oxobriges Fe(μ-O)$_2$Cr between Fe(III) and Cr(III) atoms. The IR spectra of the 100% Fe(III) and 100% Cr(III) samples display deforma-

tion bands (545, 660, 622 and 576 cm^{-1}, respectively) and stretching vibrations (468 and 446 cm^{-1}) of M–O bonds [64]. These vibrations correspond to the bands at 608, 588 and 517 cm^{-1} in the spectrum of the product of thermolysis of the coprecipitated hydroxide (spectrum 5). Such non-additive positions of all the ρ(M–O) and ν(M–O) bands and also of some other vibrations testify a mutual interference of the metals in the coprecipitated hydroxides and in the products of their thermodecomposition.

3.3. Catalytic activity of the hydroxo complexes and hydroxides in the cyclohexane or cyclopentane peroxidative oxidation

3.3.1. Homogeneous catalysis by metal hydroxo complexes

Cyclohexane oxidation by hydrogen peroxide in the absence of a catalytic agent does not proceed at ambient conditions despite of its exothermicity, due to kinetic hindrance. However, it occurs at room temperature in the presence of our Fe(III) and Cr(III) hydroxo complexes (Table 4, Fig. 7) to give the corresponding alcohol (cyclohexanol) and
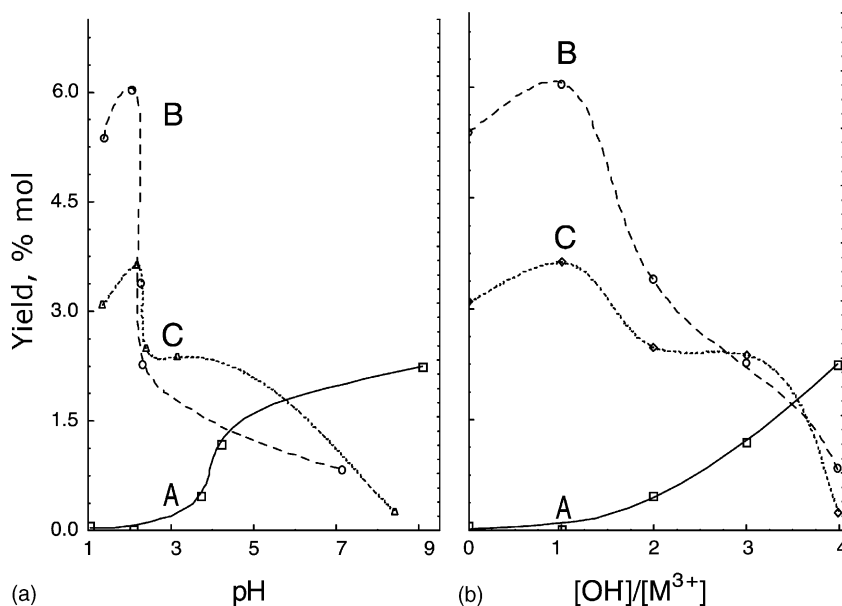

Fig. 7. Dependence of the total yield (mol%) for the peroxidative oxidation products (cyclohexanol + cyclohexanone) of cyclohexane (at ambient conditions) on pH (a) and on the neutralisation degree (b) in the following catalyst solutions: (A) Cr(III); (B) Fe(III); (C) Fe(III)–Cr(III).

ketone (cyclohexanone), the latter being the main product. The Fe(III) hydroxo complexes exhibit the greatest catalytic activity with a maximum overall yield (mol products/mol alkane) of ca. 6% with a turnover number (TON, mol products/mol catalyst) of ca. 5.6, at pH 2.0 for typical reagents molar ratios of $n(C_6H_{12}):n(H_2O_2):n[M(III)] \cong 93:88:1.0$. The Fe(III)–Cr(III) hydroxo complexes are less active (maximum yield of 3.6% at pH 2.2) and the Cr(III) hydroxo complexes are the least active ones at pH below ca. 5.5. The yield of the oxidation products is strongly dependent on pH and on the neutralisation degree of the solution of the catalytic agent (Fig. 7), and therefore it is necessary a careful control of these parameters for a maximum activity.

The chromium(III) system is inactive up to pH 3.5 (Fig. 7), i.e. when the aqua- and (to a much lesser extent) the monohydroxo complexes predominate (see the diagram of distribution of the aquahydroxo complexes depicted in Fig. 2). Hence, they do not catalyse the oxidation of cyclohexane. However, the activity of the Cr(III) system is noticeable above that pH value (Fig. 7, curve A) when the PNHC start to predominate (Fig. 2, curve 3), and increases with pH, becoming the most active one for pH above ca. 5.5 (the PNHC are than the unique species present in the chromium system). A parallelism is thus noticed between the catalytic activity of the Cr(III) system (Fig. 7, curve A) and the relative amount of the PNHC in solution (Fig. 2, curve 3), suggesting that these are (or provide) the catalytic active species, although the organic components of the catalytic system can have some effect on the distribution curves.

The maximum yield (5.2%) of cyclohexanone in the Fe(III) system is observed at pH 1.4 (Table 4), what corresponds roughly to the greatest content of the monohydroxo form $[Fe(OH)(H_2O)_5]^{2+}$ (Fig. 1, curve 2) which therefore together with $[Fe(H_2O)_6]^{3+}$ catalyses the oxidation of cyclohexane to the ketone. However, the yield of alcohol is still significant (maximum molar ratio of ketone:alcohol = 32:1) (Table 4). The maximum yield of cyclohexanol is ca. 1.7% (corresponding to the ratio ketone:alcohol = 2.6:1) and is observed at pH 2.1 when the Fe(III) PNHC are the predominant complexes (above 90%) (Fig. 1). Hence, these PNHC species appear to be (or to give) at such pH the catalytic active form for the cyclohexane ox-

idation to both alcohol and ketone. The fast drop of the catalytic activity for pH above 2.5 may result from the transfer of the entire quantity of iron to a precipitated PNHC. No additive or synergic effects resulted in the use of the binary Fe(III)–Cr(III) homogeneous system which exhibits a lower activity than the single Fe(III) or Cr(III) system, except for the pH range of ca. 2.1–5.5 when the binary system is the most active one, although still displaying a lower activity than that of the iron(III) system at lower pH values.

Thus, the most active catalytic agents for the homogeneous oxidation of cyclohexane are the Fe(III) hydroxo complexes, and the control of selectivity towards the formation of the ketone and alcohol products requires a close control of the solution pH (e.g. from pH 1.4 to 2.0 the ketone:alcohol ratio varies from 32 to 2.6).

3.3.2. Heterogeneous catalysis by metal hydroxides

The above Fe(III), Cr(III) and binary Fe(III)–Cr(III) hydroxides also exhibit catalytic activity in the peroxidative oxidation of cycloalkanes (both cyclohexane and cyclopentane were studied), and the influence of various factors such as the relative amounts of H_2O_2, acid (HNO_3) and catalyst, and the order of addition of the reagents, on the yield of the products was investigated (Tables 5–7). The amount of hydrogen peroxide has a relevant effect and $n(H_2O_2)/n(catalyst)$ molar ratio values within the 200–800 range (Tables 5 and 6) lead to much higher yields and TONs (up to 30% and 30, respectively) than those obtained when using relative amounts of H_2O_2 below 100 (Table 7, with a maximum yield of 4.3%). Moreover, the total yields of cyclohexanol and cyclohexanone when using Fe(III) hydroxide increase from 12.2 to 20.9% on changing the $n(H_2O_2)/n(catalyst)$ molar ratio from 200 to 800 (Table 5).

The yields also tend to increase with the amount of catalyst (see last three essays for the Fe(III) system) (Table 7). In the case of the Fe(III) hydroxide system, the yield of products is insignificant without addition of acid (HNO_3) to the reaction mixture, the activity being promoted by acid up to 21% yield and TON of 21, but beyond a certain acid level there occurs a yield drop probably due to the dissolution of the Fe(III) hydroxide.

Table 5
Catalytic activity of the Fe(III), Cr(III) and Fe(III)–Cr(III) hydroxides (heterogeneous systems) towards peroxidative oxidation of cyclohexane[a]

$n(H_2O_2)/n$(catalyst)	$n(HNO_3)/n$(catalyst)	Yield[b] of products		Total yield[c]	Total TON[d]	Molar ratio ketone:alcohol
		Cyclohexanol	Cyclohexanone			
Fe(III)						
200	28.8	6.46	7.98	14.44	14.4	1.2:1
400	57.8	8.65	11.51	20.16	20.2	1.3:1
200	11.5	5.39	6.82	12.20	12.2	1.3:1
400	11.5	5.71	8.81	14.52	14.5	1.5:1
800	11.5	6.49	14.42	20.91	20.9	2.2:1
800[e]	11.5	6.38	13.34	19.72	19.7	2.1:1
Cr(III)						
200	0.0	3.23	8.56	11.79	11.8	2.7:1
400	0.0	6.40	12.81	19.21	19.2	3.0:1
200	11.5	0.69	1.52	2.21	2.2	2.2:1
400	11.5	4.24	7.14	11.38	11.4	1.7:1
800	11.5	5.12	11.09	16.20	16.2	2.2:1
800[e]	11.5	5.70	10.51	16.21	16.2	1.8:1
Fe(III)–Cr(III)						
400	0.0	4.84	15.45	20.29	20.3	3.2:1
400	57.8	8.38	11.81	20.19	20.2	1.4:1
200	11.5	6.13	7.59	13.72	13.7	1.2:1
400	11.5	9.23	13.27	22.50	22.5	1.4:1
800	11.5	10.75	19.09	29.83	29.8	1.8:1
800[e]	11.5	7.11	13.98	21.09	21.1	2.0:1

[a] $n(C_6H_{12}):n$(catalyst) = 100:1.
[b] Mol product/100 mol cyclohexane.
[c] Cyclohexanol + cyclohexanone.
[d] Mol products (cyclohexanol + cyclohexanone)/mol catalyst.
[e] Different sequence of addition of reagents was used (see Table 7).

In contrast, the catalytic activity of the Cr(III) hydroxide, which decreases with the addition of acid, is maximum without acid addition although without reaching the level of activity of Fe(III) hydroxide in acidic medium. However, Cr(III) hydroxide displays a higher selectivity towards the formation of the ketone than Fe(III), in the cyclopentane oxidation (Table 6).

Interestingly, a *synergic effect* of the metal hydroxides is observed in the case of cyclohexane. Hence, for $n(C_6H_{12}):n(H_2O_2):n(HNO_3):n$(catalyst) = 100:800:11.5:1, the total yield for the mixed system is 29.8% whereas for the Fe(III) and the Cr(III) ones is 20.9 and 16.2%, respectively (Table 5). Similarly, for a lower amount of H_2O_2 (400:1 relatively to the catalyst), those values are of 22.5 (mixed system), 14.5 (iron hydroxide) and 11.4% (chromium hydroxide) (Table 5).

The obtained results on the physicochemical and catalytic properties of the binary hydroxide system indicate that its catalytic activity is conditioned by a chemical interaction between the Fe(III) and Cr(III) centres in the structure of the solid.

The order of addition of the reagents usually does not appear to have an appreciative effect, but for the binary system a better yield is obtained by adding first H_2O_2 to the catalyst suspension in CH_3CN than when the acid is the first reagent to be added (see two last essays for each metal system in Table 5).

Table 6
Catalytic activity of the Fe(III), Cr(III) and Fe(III)–Cr(III) hydroxides (heterogeneous systems) towards peroxidative oxidation of cyclopentane

$n(H_2O_2)/n$(catalyst)	$n(C_5H_{10})/n$(catalyst)	$n(HNO_3)/n$(catalyst)	Yield[a] of products		Total yield[b]	Total TON[c]	Molar ratio ketone:alcohol
			Cyclopentanol	Cyclopentanone			
Fe(III)							
200	100	0.0	0.00	0.00	0.00	0.0	–
200	100	28.8	5.59	7.53	13.12	13.1	1.3:1
200	50	0.0	0.00	0.00	0.00	0.0	–
200	50	28.8	8.09	10.88	18.97	9.5	1.3:1
Cr(III)							
200	100	0.0	1.58	7.57	9.15	9.2	4.8:1
200	100	28.8	0.00	0.00	0.00	0.0	–
200	50	0.0	1.19	13.27	14.46	7.2	11.2:1
200	50	28.8	0.12	0.00	0.12	0.0	–
Fe(III)–Cr(III)							
200	100	0.0	0.25	6.72	6.97	7.0	27.3:1
200	100	28.8	4.04	5.46	9.50	9.5	1.4:1
200	50	0.0	1.08	11.55	12.63	6.3	10.7:1
200	50	28.8	4.56	12.17	16.73	8.4	2.7:1

[a] Mol product/100 mol cyclopentane. Values lower than 0.005 are not given.
[b] Cyclopentanol + cyclopentanone.
[c] Mol products (cyclopentanol + cyclopentanone)/mol catalyst. Values lower than 0.05 are not given.

Table 7
Catalytic activity of the Fe(III), Cr(III) and Fe(III)–Cr(III) hydroxides (heterogeneous systems) towards peroxidative oxidation of cyclohexane

$n(H_2O_2)/n$(catalyst)	Mass of catalyst (g)	V (HNO$_3$) (ml)	Yield[a] of products		Total yield[b]	Molar ratio ketone:alcohol
			Cyclohexanol	Cyclohexanone		
Fe(III)						
28.3	0.010	0.00	0.006	0.015	0.02	2.5:1
94.3	0.010	0.00	0.003	0.006	0.01	2.0:1
28.3	0.010[c]	0.10	0.022	0.059	0.08	2.7:1
94.3	0.010	0.10	0.178	0.299	0.48	1.7:1
28.3	0.010	0.20	0.020	0.041	0.06	2.1:1
28.3	0.010	0.30	0.019	0.046	0.07	2.4:1
28.3	0.020	0.10	0.104	0.142	0.25	1.4:1
28.3	0.030	0.10	0.134	0.188	0.32	1.4:1
28.3	0.050	0.10	0.224	0.328	0.55	1.5:1
Cr(III)						
27.3	0.010	0.00	0.132	0.701	0.83	5.3:1
91.0	0.010	0.00	1.466	1.425	2.89	1.0:1
27.3	0.010[d]	0.10	0.020	0.006	0.03	0.3:1
27.3	0.050	0.10	0.008	0.009	0.02	1.1:1
Fe(III)–Cr(III)						
27.8	0.010[e]	0.00	0.182	0.723	0.91	4.0:1
92.7	0.010	0.00	1.083	3.185	4.27	2.9:1

[a] Mol product/100 mol cyclohexane.
[b] Cyclohexanol + cyclohexanone.
[c] $n(C_6H_{12}):n(H_2O_2):n(HNO_3):n(Fe(OH)_3) = 98.8:28.3:23.7:1$.
[d] $n(C_6H_{12}):n(H_2O_2):n(HNO_3):n(Cr(OH)_3) = 95.3:27.3:22.9:1$.
[e] $n(C_6H_{12}):n(H_2O_2):n(FeCr(OH)_6) = 97.1:27.8:1$.

4. Conclusions

We have prepared and applied aquahydroxo complexes and metal hydroxides as catalysts for the homo- or heterogeneous, respectively, peroxidative oxidation of cyclohexane and cyclopentane to the corresponding alcohols and ketones.

For the homogeneous systems, the iron(III) species behave as the best catalysts, and the pH has been optimised for the best product yields and selectivity (highest ketone/alcohol molar ratio). The forms of the hydroxo complexes that are active (or that generate the active ones) have been recognised, but no synergic effect has been observed when using simultaneously the complexes of both metals.

The heterogeneous metal hydroxide catalysts are more active than the homogeneous ones, and the occurrence of a *synergic effect* in cyclohexane oxidation has been recognised for the binary Fe(III)–Cr(III) hydroxide system which behaves as the best catalyst, with a maximum yield of ca. 30% (TON = 30).

In addition, this work has also allowed to establish the equilibrium compositions of the catalysts or their precursors, obtained as the products of the polynuclear hydrolysis in Fe(III), Cr(III) and Fe(III)–Cr(III) nitrate solutions, as a function of pH and neutralisation degree. Fe(III)–Cr(III) hydroxides and products of their thermolysis were prepared and characterized by various methods, i.e. potentiometric titration, thermal analysis, IR spectroscopy and X-ray powder diffraction. The maintenance of an Fe(III)–Cr(III) interaction in the sequence "dissolved aquahydroxo complexes—coprecipitated hydroxides—composite oxides" has also been recognised.

The application of the above hydroxo catalysts to other functionalization reactions of alkanes is under way in our group.

Acknowledgements

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