Catalysis Letters Vol. 82, No. 1–2, September 2002 (©2002)

Synthesis and characterization of boron hydrotalcite-like compounds as catalyst for gas-phase transposition of cyclohexanone-oxime

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Received 17 December 2001; accepted 9 April 2002

Hydrotalcite-like compounds with boron anions in the interlayer were obtained using a coprecipitation method. The effect of different pH values during the preparation was investigated and the effect on crystallinity and phase distribution studied. The influence of different methods of acidity regulation was also analyzed. The efficiency of synthesis of boron-containing anionic clays was evaluated, and the good thermal stability of the materials was noted. Surface characteristics were determined by X-ray photoelectron spectroscopy and correlated to the bulk properties obtained by X-ray diffraction and ^{27}Al and ^{11}B MAS NMR. The samples tested in gas-phase Beckmann rearrangement showed caprolactam formation, and the results were related to the surface features.

KEY WORDS: hydrotalcite-like compounds; boron; XPS; MAS NMR; Beckmann rearrangement.

1. Introduction

Hydrotalcite-like compounds (HTlc) are characterized by a layered structure, where the positive charge in the Mg/Al hydroxide sheets is neutralized by charge-balancing anions, normally CO_3^{2-} and/or hydrogen bonding. The CO_3^{2-} in the interlayer space can be substituted by other inorganic and organic anions, forming new hydrotalcite-like materials. The synthesis of borate-pillared hydrotalcites appears very interesting because they should have acid sites of intermediate Brønsted strength which promote acid reactions, like the Beckmann rearrangement. The Beckmann rearrangement utilizing heterogeneous catalysts in the gas phase is one of the most attractive new technologies [1]. The reaction requires the presence of weak Brønsted acid sites to successfully convert cyclohexanone-oxime to caprolactam [2–5], while strong acid sites promote fragmentation reactions. As a matter of fact, major by-products of the reaction are generated by fragmentation or hydrolysis of cyclohexanone-oxime and by condensation like heavy compounds and tars.

Boron is known to allow the selective conversion of the oxime to the lactam [6–21]. However, Curtin *et al.* [16] observed a loss of B_2O_3 of boria supported on alumina either during reaction or thermal treatments, while Albers *et al.* [22] synthesized a boron-containing zeolite which is characterized by a non-pronounced and irreversible deboration effect on its surface and a service time up to more than one year. For this reason hydrotalcite-like materials based on boron were prepared. The structural stability of the mixed oxides let this catalyst be suitable for rearrangement in the gas phase. The introduction of borates within the layers should lock the active phase, decrease its partial loss by leaching phenomena and provide the catalysts with a suitable acidity. A lot of experimental works [1,4,6,7] state that, in silicon-containing materials such as zeolites, the contribution of nests of silanols or vicinal silanol groups, of extremely weak acidity, is of basic importance for good catalytic performance. The positive effect of boron is, in general, recognized [6]. According to Curtin *et al.* [9], boron-modified alumina of intermediate acid strength favors the formation of caprolactam. In this paper the results of a study on the characterization and activity of anionic clays containing borates are reported. Several samples were prepared by coprecipitation according to refs. [20,23,24], but changing some preparation parameters. The effect of different pH values of the solution on the catalyst final structure was investigated as well as the way pH was regulated. A detailed characterization was carried out in order to determine the structure and the physicochemical properties of the catalysts. The catalytic activity of the samples was investigated and related to the properties of the materials.

2. Experimental

Hypotalcite-like compounds were prepared starting from a solution of $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$

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(Mg/Al = 1.9) which is added to an aqueous solution containing an excess of boric acid. NaOH 0.3 M was then utilized to regulate the solution pH. The precipitate was kept under mixing for 15 h, then filtered and washed with deionized water, dried under vacuum at 80 °C and eventually calcined at 400 °C for 4 h.

Boron elemental analysis was made by mean of a Uvikon 860 spectrophotometer, while magnesium and aluminum elemental analysis was carried out using a Philips PU 9100 spectrophotometer for atomic absorption. Powder X-ray diffraction (XRD) was carried out using a PW 1050/81 Philips diffractometer. X-ray photoelectron spectroscopy (XPS) spectra were obtained by means of a Leybold Haraeus LHS 10 with the Al K_α radiation at 1486.6 eV. Binding energies were measured by reference to the Al(2p) peak at 74.8 eV. The ^{27}Al and ^{11}B spectra were recorded on a Brucker ASX 400 spectrometer working at 104.2 MHz (^{27}Al) and 128.3 MHz (^{11}B). ^{27}Al spectra were recorded with a spinning frequency of 13 500 Hz, single pulse and a repetition time of 2 s, the reference being $Al(H_2O)_6^{3+}$. ^{11}B NMR spectra were recorded with a spinning frequency of 12 500 Hz, single pulse and a repetition time of 10 s, the reference being $BF_3{\cdot}OEt_2$.

Catalyst texture was determined by means of nitrogen adsorption at −196 °C with a Micromeritics ASAP 2010 porosimeter after treatment of the samples at 200 °C under vacuum. Pore-size distribution was obtained by the Barrett–Joyner–Halenda (BJH) method.

Thermogravimetric analysis (TGA) was carried out on a TA instruments TGA 2050 model. Weight losses were recorded in air flow, in the temperature range 30–900 °C.

Beckmann rearrangement was carried out in a glass fixed-bed reactor having an internal diameter of 4 mm. The catalyst in 30–40 mesh pellets was introduced in a tubular glass reactor, packed with inert material. The temperature of the catalytic bed was set at 350 °C (according to the literature [25] this is the temperature at which the highest yield is obtained) and at a weight hourly space velocity (WHSV) = 1.21 h^{-1}. A solution of cyclohexanone-oxime (4 mol%) in toluene was supplied by a microfeeder at a constant flow rate, nitrogen (52 mol%) being the carrier. The products were determined by a GCD gas chromatograph with flame electron ionization detector (FID).

3. Results and discussion

3.1. Structure dependence on pH value and method of pH regulation

One of the peculiarities of hydrotalcite-like compound preparation with boron oxides as intercalated anions is the possibility of selecting different boron species as a function of the pH values of the starting solution. Bhattacharyya and Hall [20] and Farmer [26] reported pH range (figure 1) where several boron anions are stable and present in substantial amounts. The same authors specified the pH of preparation for the species $[B_3O_3(OH)_4]^-$ and $B(OH)_4^-$. The former is predominant in the range between 8.3 and 9.0, the latter at pH ≥ 11.0 because of the hydrolysis phenomena which occur on different kinds of borates present at lower basicity values [20,26]. In order to introduce as much boron as possible in the structure, the preparations should be mostly set within the range 8.3 ≤ pH ≤ 9.0 so that for each positive charge attributed to aluminum, three boron atoms are expected to be inserted.

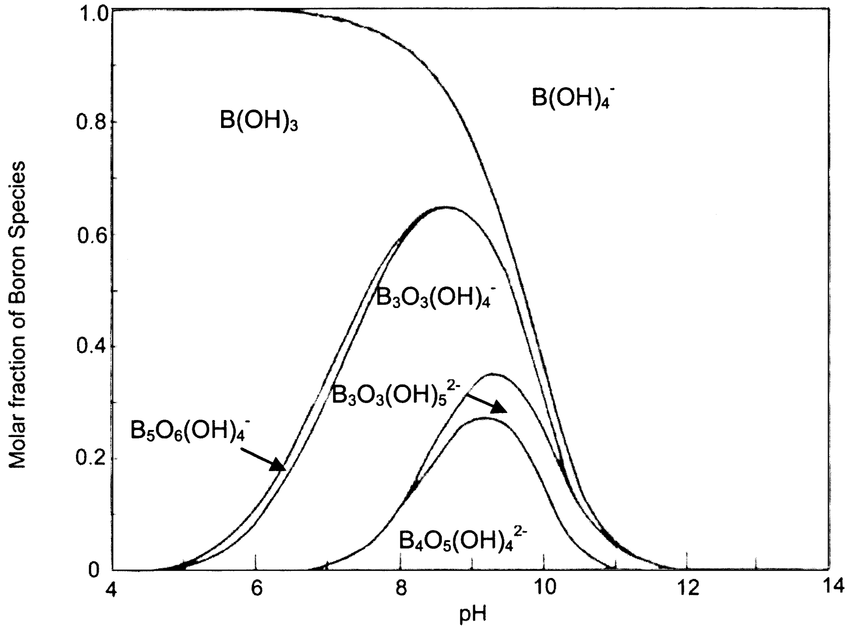

Figure 1. Distribution of boron species as a function of solution pH.

Table 1
Boron weight percentage content and molar ratio of atoms on the basis of pH regulation method and pH value

Sample	pH	pH regulation	Mg/Al	B/Al	B (wt%)
HTlc-1	7.5	Step by step	0.9	0.9	4.7
HTlc-2	9.0	Step by step	1.2	0.9	5.3
HTlc-3	11.0	Step by step	1.4	0.7	4.2
HTlc-4	9.0	Final	1.3	0.9	5.0

Table 1 shows the dependence of the composition and boron content on the pH value and pH regulation method for three samples prepared at different pH values.

The largest boron amount was found in the material synthesized at pH = 9.0. However, the boron amount in all the samples was low and the theoretical ratio B/Al = 3.0 was never achieved. This can be related to the fact that the desired boron species was not exclusively selected. In addition, the catalyst final structure is also dramatically affected by the pH values; in fact, sample crystallinity increases with the increasing dropwise controlled pH. In figure 2, XRD patterns of dried HTlc synthesized at different pH values are shown.

Sample HTlc-1, obtained by setting the solution pH at 7.5, is characterized by a rather low crystallinity but shows a minimum amount of HTlc. The first peak of the pattern corresponds to a *d* spacing of 8.07 Å. The sheet thickness of hydrotalcite is about 4.8 Å, so the interlayer space is estimated to be 3.3 Å. This space is consistent with the insertion of monoborate anion $[B(OH)_4]^-$ or triborate anion $[B_3O_3(OH)_4]^-$ parallel to the cationic layer. Sample HTlc-2 (pH = 9.0) has a multiphase pattern; in this case two peaks corresponding to *d* spacing d_{003} are identified at 10.78 and 8.07 Å. Those can be related to hydrotalcite-type phases containing two different kinds of anions in sequence, $[B_3O_3(OH)_4]^-$ and $[B(OH)_4]^-$. Sample HTlc-3 (pH = 11) shows the typical crystalline hydrotalcite pattern: the prevalent phase shows the first peak at 7.98 Å, caused by the insertion of monoborate $[B(OH)_4]^-$ anions.

XRD analysis, by itself, cannot exactly determine the different species of anions inserted in the layers; moreover, it does not seem possible to exclusively introduce between the cationic layers a single kind of borate anion only by carefully selecting the solution acidity. This phenomenon might be caused by the simultaneous presence of several species of borate anions at a selected pH and by the presence of a local pH that occurs during the formation of the layers. The greatest difference is found at higher basicity values (sample HTlc-3) where a single species inserted in the interlayer is produced and a highly crystalline material is formed.

To better investigate the pH influence some samples were prepared with a different pH regulation method. An HTlc structure was formed adding a quantity of soda to reach, at the end of the precipitation of the cationic solution, pH = 9 (HTlc-4) and compared with the materials prepared controlling dropwise the pH at 9 (HTlc-2). They are both multiphasic materials but, while dried HTlc-2 is characterized by a double peak corresponding to the interlayer distance, sample HTlc-4 shows a d_{003} peak at 8.8 Å which is characterized by a slight shoulder at 10.8 Å, as shown in figure 3. Those phases can be respectively related to monoborate anion $[B(OH)_4]^-$ and to triborate anion $[B_3O_3(OH)_4]^-$. After calcination of the HTlc-2 and HTlc-4 samples, structural differences are homogenized and the evolution toward a similar phase can be observed. The double-phased peaks are turned into a single reflection having a *d* spacing value of 6.9 Å due to the dehydration of the materials.

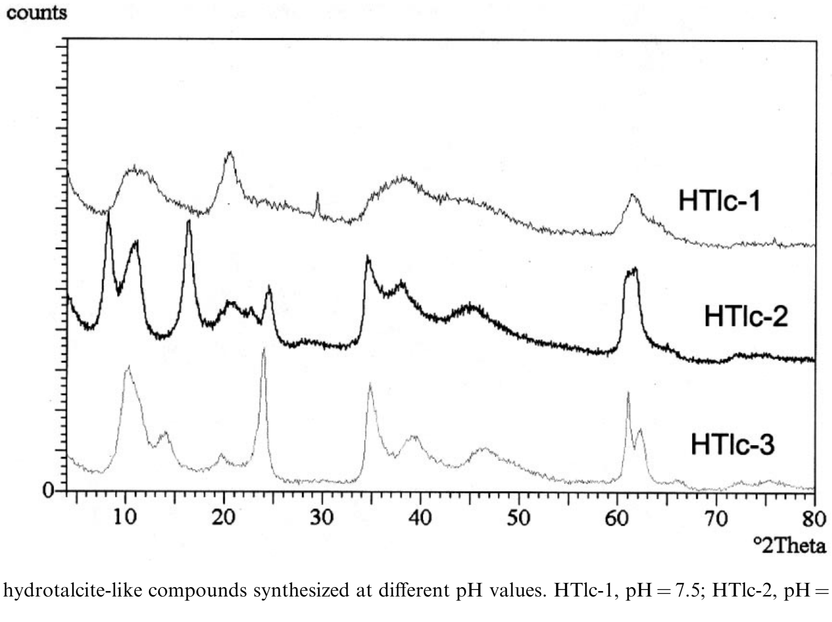

Figure 2. XRD patterns of hydrotalcite-like compounds synthesized at different pH values. HTlc-1, pH = 7.5; HTlc-2, pH = 9.0; HTlc-3, pH = 11.

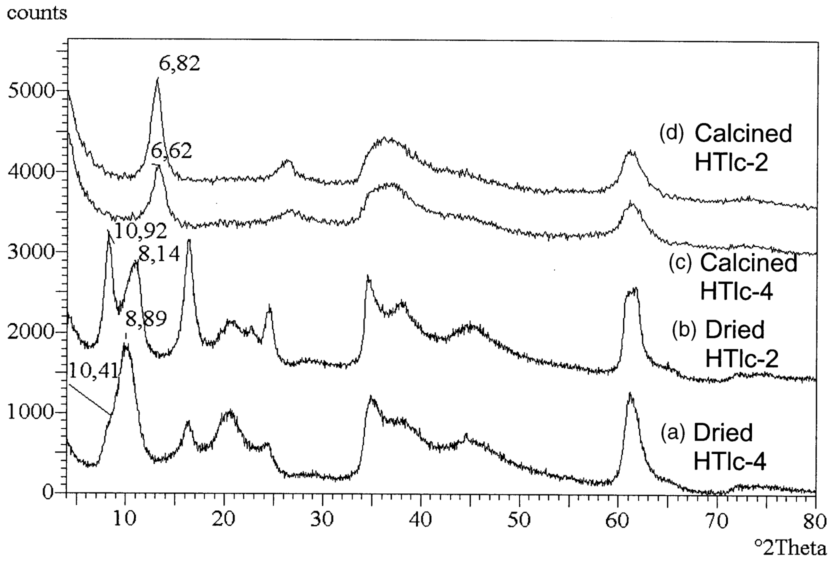

Figure 3. XRD patterns of dried and calcined samples HTlc-2 and HTlc-4: (a) dried HTlc-4; (b) dried HTlc-2; (c) calcined HTlc-4; (d) calcined HTlc-2.

In addition, samples HTlc-2 and HTlc-4 exhibit different surface areas and pore-volume values, but a similar pore-size distribution and pore-dimension range. HTlc-2 is characterized by the rather low surface area of 29 m^2/g, while sample HTlc-4 exhibits a higher surface area (90 m^2/g). This can be explained with the higher pH values reached during HTlc-4 preparation that promote the introduction of carbonates. The elimination of carbonates during the calcination phase causes the formation of an additional porosity in the material with a consequent increase in surface area. The adsorption and desorption isotherms of nitrogen show an uptake at intermediate relative pressures, typical of mesoporous materials, as shown in figure 4.

Pore-size distribution is characterized by a wide distribution of pores, centered mainly in the mesoporous range: average pore diameter following the BJH equation is 150 Å for HTlc-2 and 170 Å for HTlc-4.

XPS studies showed different surface atomic distribution on samples synthesized at $\mathrm{pH} = 9.0$ and $\mathrm{pH} = 11.0$ in comparison with that found in the bulk (table 2). Bulk atomic composition was determined by the atomic absorption method. The samples, prepared at $\mathrm{pH} = 9.0$, are characterized by a heterogeneous distribution between surface and bulk which mainly involves magnesium and aluminum atoms. HTlc-3, on the contrary, shows a homogeneous distribution of the above-mentioned atoms.

In particular, samples prepared at $\mathrm{pH} = 9.0$ are characterized by a larger boron amount than samples prepared at $\mathrm{pH} = 11.0$, but an Mg/Al ratio on the bulk significantly lower than the ratio found on its surface. The binding energy of Al species is characterized, both in the dried and calcined samples, by a single value. Consequently the existence of a single aluminum species or two different species having the same coordination but

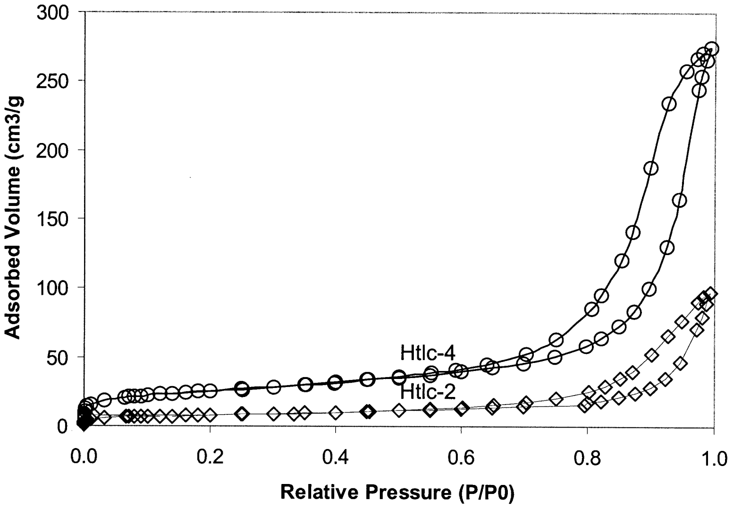

Figure 4. Isothermal uptake of nitrogen at −196 °C of boron-containing hydrotalcite-like compounds synthesized according to coprecipitation methods.

Table 2
Atomic ratio values referred to the surface and bulk of the dried catalysts

Sample	Composition		Composition
HTlc-2 surface	Mg 52.3%	Bulk	Mg 39.0%
	Al 21.8%		Al 32.8%
	B 25.9%		B 28.2%
HTlc-3 surface	Mg 59.0%	Bulk	Mg 55.0%
	Al 26.8%		Al 28.1%
	B 14.2%		B 16.9%
HTlc-4 surface	Mg 50.8%	Bulk	Mg 41.0%
	Al 20.8%		Al 31.7%
	B 28.4%		B 27.3%

Table 3
Atomic ratio values referred to the surface and bulk of the calcined catalysts

Sample	Composition		Composition
HTlc-2 surface	Mg 32.8%	Bulk	Mg 54.4%
	Al 28.7%		Al 20.5%
	B 38.5%		B 25.1%
HTlc-4 surface	Mg 35.5%	Bulk	Mg 52.6%
	Al 30.3%		Al 19.5%
	B 34.2%		B 27.9%

a different chemical neighborhood can be supposed. Magnesium oxide is often located on the catalyst surface, but its quantity decreases with the depth of the layers. For these reasons, greater amounts of magnesium are found on the very first layers to the point that the external layer is mainly covered by magnesium crystals.

Boron anions within the investigated samples are always characterized by an equal value of binding energy, and a diminution of that value (0.4 eV) is observed between the dried and the calcined sample. As the binding energy is smaller than that of H_3BO_3 and B_2O_3 [27,28], boron oxides inserted within the structure are not a segregated phase but are part of the clay lattice. It is, therefore, still not possible to determine the exact identity of those boron species as the XPS signals are quite symmetric. For this reason a single type of coordination could probably be present, even though it is not possible to exclude the presence of several boron anions having the same coordination in a different chemical surrounding. XPS studies did not show any compositional difference in the surface and in the bulk of the two calcined catalysts (table 3), and the binding energy value did not allow any conclusion different from that mentioned above.

Aluminum (^{27}Al MAS NMR) and boron (^{11}B MAS NMR) solid-state nuclear magnetic resonance spectroscopy can be useful techniques to better focus the element characteristics in hydrotalcite-like compounds [29,30]. HTlc-2 and HTlc-4 have been taken as reference materials and ^{27}Al MAS NMR was carried out on the dried sample. The analysis of HTlc-2 shows the presence of a single isolated peak at 9.54 ppm attributed to octahedral rather than perturbed aluminum.

The calcined sample shows the presence of two peaks at 62.0 and 8.8 ppm (figure 5). Two hypotheses can be formulated [31]:

1. The peak at 8.8 ppm is caused by the octahedral aluminum and the one at 62.0 ppm by the tetrahedral aluminum coordination.

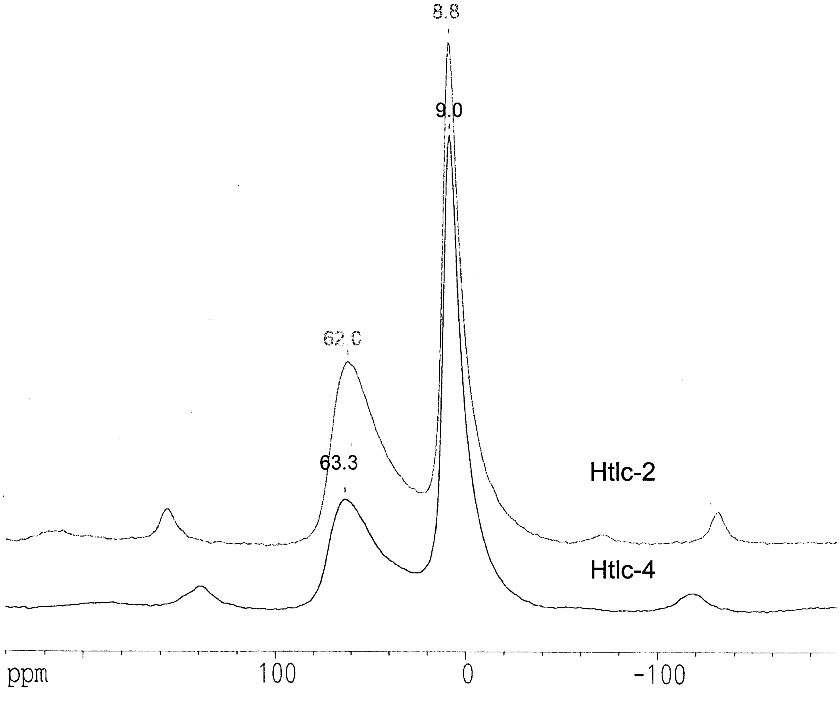

Figure 5. ^{27}Al MAS NMR spectrum of calcined HTlc-2 and HTlc-4 samples.

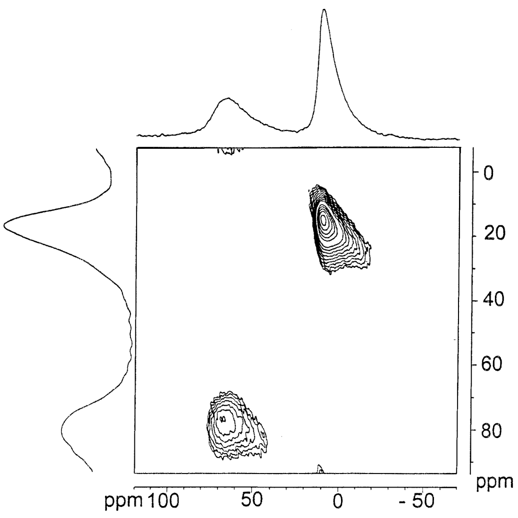

Figure 6. ^{27}Al MQ MAS NMR diagram of calcined HTlc-4 sample.

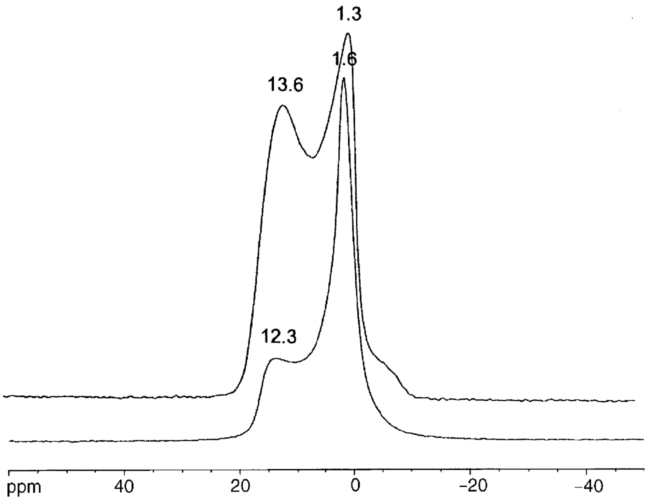

Figure 7. Thermal behavior of dried and calcined HTlc-2.

2. Both peaks are due to an octahedral species, but the second peak is weakened by the perturbation of its chemical surrounding because of interactions between boron and aluminum bonded by oxygen atoms formed during calcination. This phenomenon could cause layer disorganization of hydrotalcite-like materials and, as a consequence, their low crystallinity.

In comparison with the reference molecule, aluminum atom's electronic surrounding is weakened by the proximity of closer atoms. As a matter of fact, the reference oxygen $(Al(H_2O)_6)^{3+}$ is surrounded by two hydrogen atoms while the oxygen bonded to the aluminum atoms in the calcined materials is surrounded by boron atoms.

The analysis of the HTlc-4 dried sample is similar to that of HTlc-2, and the same for the calcined samples. Consequently the different pH regulation method seems not to affect the final aluminum species. The peak at 63.3 ppm seems to be split. To verify whether quadrupolar interactions might be present, a ^{27}Al MQ MAS NMR study was carried out and the presence of two non-coupled aluminum species was detected (figure 6). This result still does not allow a definite conclusion.

^{11}B MAS NMR analysis of dried HTlc-2 is characterized by the presence of two peaks at 1.6 and 13.6 ppm as reported in figure 7. According to Dumeignil *et al.* [31], the first peak is due to tetrahedral coordinated boron anions out of the HTlc lattice, while the second one is typical of trigonally coordinated species which are usually located in the 17 ppm zone. In this case the BO_3 species undergoes a magnetic field shift toward lower values due to the electrostatic interaction with aluminum atoms.

The calcined samples HTlc-4 and HTlc-2 show an increase of quadrupolar interaction and also of the same magnetic field shift observed in the dried samples, as shown in figure 7. Comparing the mentioned samples with the dried samples, an increase of magnetic field shift can be observed in both cases, corresponding to the BO_3 species. This is due to the internal electric field gradient which is generated as a consequence of aluminum atom perturbation. For this reason, after calcination and layer disorganization, the BO_3 species is the most abundant and it interacts with octahedral aluminum; magnetic field shift takes place both for boron and aluminum species, while the BO_4 species undergoes only a weak interaction with a few aluminum atoms. The evolution of tetrahedrally coordinated boron to trigonally coordinated boron after calcination is an effect already observed in boron-containing zeolites [32].

The thermal behavior of HTlc prepared is rather complex. The dried samples are characterized by an initial weight loss in two steps in the range between 100 and 200 °C, as shown in figure 8 for the HTlc-2 sample, corresponding to adsorbed and interlayer water with retention of the material structure. A second two-step weight loss occurs in the range between 450 and 600 °C, this being attributed to the dehydroxylation of both the cation and anion layers; this points out the peculiar higher thermal stability of HTlc with boron oxides as anions, which completely evolves to mixed-oxides structure at a temperature near 600 °C. In fact, at around 700 °C a segregated B_2O_3 phase is probably formed. Finally at 830 °C the evolution towards a spinel + MgO-type phase is completed. The weight loss and the temperatures of these transitions depend on several factors such as the Mg(II)/Al(III) ratio and the kind and amount of anions.

The sample calcined at 400 °C shows only a dehydration of materials due to the thermal treatment with no change of the phases, as reported in figure 7. In fact, the structure evolution with temperature is the same as that of the dried sample.

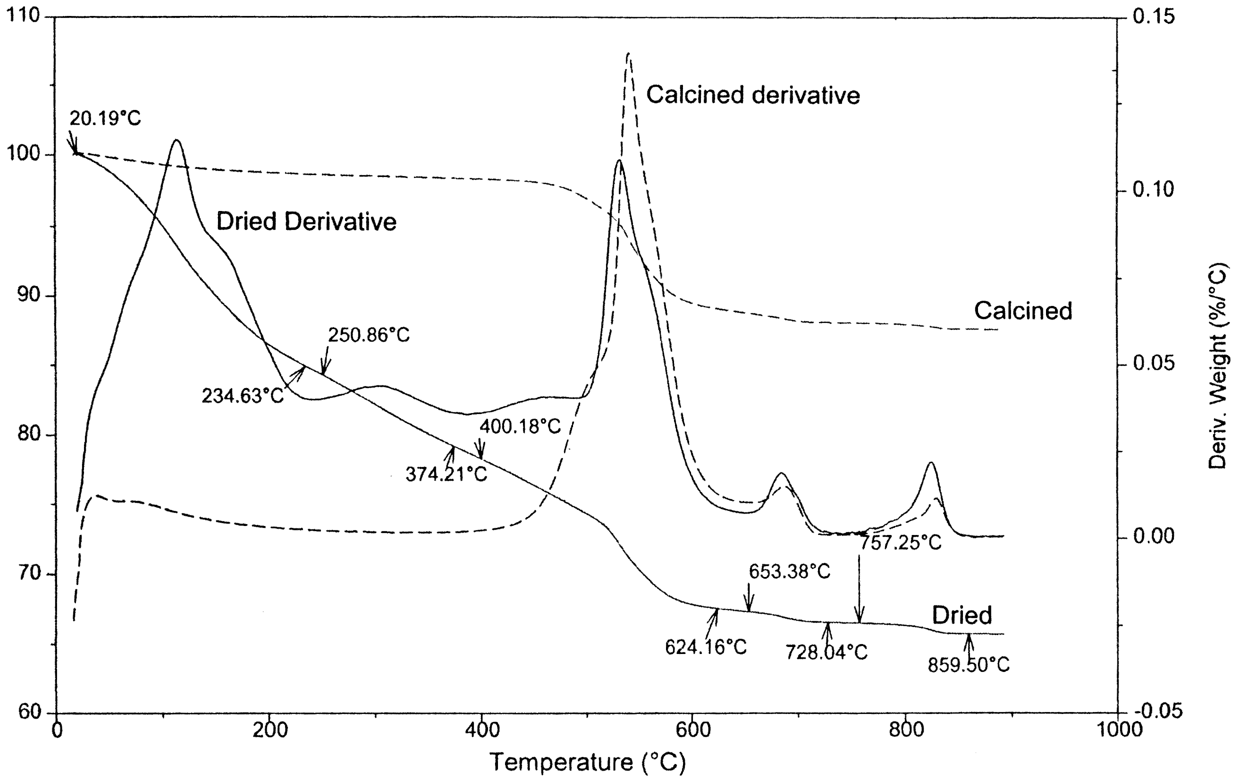

Figure 8.

3.2. Catalytic activity

The HTlc-2 and HTlc-4 calcined samples were tested in the Beckmann rearrangement reaction in the gas phase. The samples are active in the reaction and HTlc-4 shows a higher initial cyclohexanone-oxime conversion than that of HTlc-2, as reported in figure 8. This is attributed to the higher surface area and to the more easily reachable acid sites of the first material. However, these acid sites are mostly non-selective ones, and in fact the HTlc-4 catalyst undergoes a fast deactivation and caprolactam selectivity is sensibly lower than that of sample HTlc-2, even if it is rather low also in this latter case.

The average low caprolactam selectivity of HTlc-like materials can be attributed to three main factors:

1. the low availability of boron atoms on the catalyst surface according to XPS results,
2. the low quantity of boron atoms introduced in the lattice,

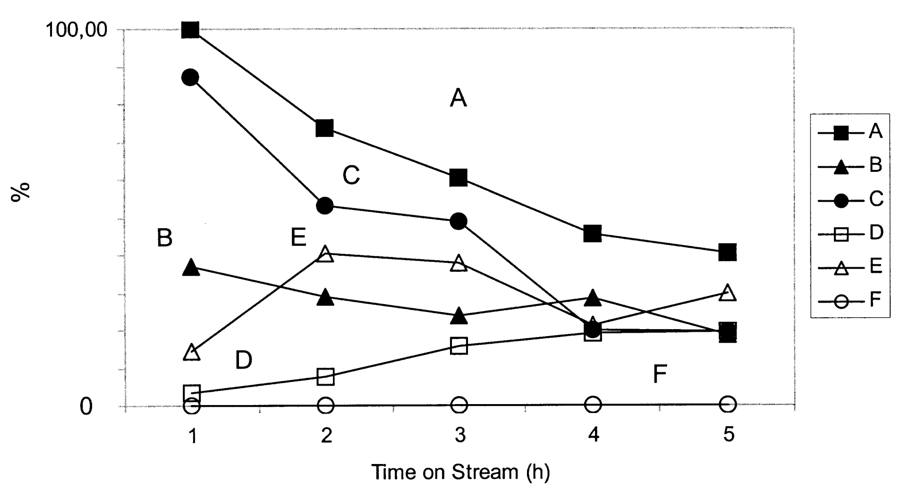

Figure 9. Catalytic behavior of HTlc-2 and HTlc-4 compared with Mg/Al mixed oxide. A: oxime conversion of HTlc-4; B: oxime conversion of HTlc-2; C: oxime conversion of Mg/Al; D: caprolactam selectivity of HTlc-4; E: caprolactam selectivity of HTlc-2; F: caprolactam selectivity of Mg/Al.

3. the electrostatic interactions between anionic and cationic layers and the occurring grafting reactions that modify the original acidity of the boron anions.

The higher caprolactam selectivity in sample HTlc-2 might be attributed to the higher amount of surface boron detected by XPS analysis. Further evidence of the slightly different acid properties of the two samples is found in cyclohexanone selectivity, which is relatively higher in sample HTlc-4. Therefore, catalyst HTlc-4 seems to be characterized by a greater amount of stronger acid sites, while HTlc-2 has a wider and more tailored acid-site distribution.

The catalytic activity of the two boron-containing HTlc-like materials was compared with the mixed oxide Mg/Al phase without borates, characterized by a high-surface-area value of 221 m^2/g.

Cyclohexanone-oxime conversion values of the mixed oxide phase (Mg/Al) stay in between the values found for the other catalysts. This behavior is promoted by the higher surface area of the mixed oxide, even if in the case of the HTlc-4 sample the presence of boron atoms together with a slightly high surface area allow a higher conversion of the reactant. However, the mixed oxide does not form caprolactam, even in traces. This means that the presence of boron atoms is necessary and leads to the formation of acid sites able to produce caprolactam.

Catalytic performances of HTlc-like materials are, however, still far from those obtained with boron-based materials prepared by conventional methods or with boron zeolites [1]. Röseler *et al.* [11] reported a cyclohexanone-oxime conversion of 100% and caprolactam selectivity up to 95% for B-MFI zeolites at 300 °C and 0.1 bar. Recently Ichihashi and Kitamura [7] claimed a cyclohexanone-oxime conversion of 100% and a caprolactam selectivity of more than 95% on modified silicalites.

4. Conclusions

Boron-containing HTlcs are an interesting class of anionic clays for their good thermal stability, because of the retention of the HTlc structure that can still be detected at temperatures above 500 °C and for their potential catalytic features due to the presence of borates. These materials were successfully prepared, but their structure and the boron content are dramatically affected by the pH of the preparation. In fact, by selecting the pH range it is possible to preferentially promote the insertion of a boron anion species. Furthermore, the samples' crystallinity increases with increasing pH of the preparation solution.

HTlcs obtained by dropwise pH regulation are characterized by a different phase distribution with respect to the pH regulation at the end of coprecipitation, but most of all by low surface areas and different acid properties.

Surface studies showed the presence, on the first clay layer of the dried samples, of large amounts of magnesium oxides. This causes, as a drawback, a small amount of boron atoms on the catalyst surface of the dried samples, while in the calcined samples the amount of boron atoms is higher. A comparison between the results obtained from ^{27}Al MAS NMR, ^{11}B MAS NMR and XPS studies shows the presence of two non-coupled boron species with the same coordination but a different chemical surrounding. BO_3 seems to be the most abundant species in the calcined samples and shows a strong interaction with aluminum atoms. On the contrary, BO_4 undergoes only a weak interaction with few aluminum atoms.

The catalysts obtained from HTlc prepared with different pH regulation show the same caprolactam yield but different cyclohexanone-oxime conversion and caprolactam selectivity as a consequence of a different acid site distribution with respect to an Mg/Al mixed oxide, and the introduction of borates in the interlayer successfully produces a certain amount of the desired product. In comparison with low boron content, the performances of the catalyst obtained by anionic clays are poorer than expected, because of the loss of acidic properties due to grafting reactions during thermal treatments and to the low surface availability of boron anions.

Acknowledgments

The authors would like to thank those who contributed to this research: Dr. C. Faenza who contributed to the synthesis of HTlc materials and catalytic tests, Mrs. Catherine Meliet for MAS NMR analysis and Mrs. Virginie Moineau for XPS tests.

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