

# Basic Properties of the Mixed Oxides Obtained by Thermal Decomposition of Hydrotalcites Containing Different Metallic Compositions

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Carbonated layered double hydroxides (LDHs) containing Al, Fe, or Cr in a Mg(OH)<sub>2</sub> matrix or Al dissolved in hydroxides of Mg, Cu, Ni, Co, or Zn are used as precursors of basic catalysts. Decarbonation is studied by thermal analysis. The average basic strength, evaluated by the decarbonation temperature, is related to the partial charge of oxygen in the LDHs obtained from the Sanderson theory of electronegativity. The enthalpy of adsorption of CO<sub>2</sub> on the resulting mixed oxides is measured by calorimetry. A homogeneous surface is generally observed for CO<sub>2</sub> adsorption, with initial heats of adsorption close to those reported for MgO. The number of sites determined by this method is proportional to the rate constants for β-isophorone isomerisation, suggesting that both techniques measure surface properties. The layered structure in which OH<sup>-</sup> is the compensating anion can be re-formed by hydration. This process does not appreciably change the adsorption of CO<sub>2</sub>; thus, oxygens and hydroxyls show similar basic strengths in this case. © 2000

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**Key Words:** layered mixed hydroxides; basicity; enthalpy of adsorption; carbon dioxide; isophorone isomerization.

## INTRODUCTION

The replacement of liquid acids and bases by solids as catalysts in organic reactions is a requisite for better preservation of the environment (1, 2). While the research on solid acid catalysts was driven by oil refining to the discovery of a large number of systems including zeolites, clays, mixed oxides, and sulfates, only a few solid bases are yet available. Among them, layered double hydroxides (LDHs) or hydrotalcite-like materials are interesting because they can give wide-pore solids which would be able to accept the substrates of organic chemistry. Calcination of LDH yields mixed oxides which are basic solids. The properties of those can be tailored by the nature of the cations, the compensating anions, and the calcination temperature (3–6).

The ideal formula of the original LDH is  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} [A_{x/m}^{m-}] \cdot nH_2O$ , accounting for the lamellar structure whose sheets, positively charged, associate in

an appropriate ratio ( $1.5 < M^{2+}/M^{3+} < 4$ ) different divalent (Mg<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, etc.) and trivalent cations (Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ga<sup>3+</sup>, etc.). The synthesis of these LDH precursors is well-documented (7–11). They are usually used as precursors of the actual catalyst. Indeed, the decarbonated materials obtained by appropriate activation of the corresponding LDH catalyzed a variety of organic transformations such as aldol condensation (6, 13, 14), olefin isomerisation (8), nucleophilic halide exchange (12), alkylation of diketones (15), epoxidation of activated olefins with hydrogen peroxide (16), Claisen-Schmidt condensation (17), selective reduction of unsaturated ketones/aldehydes by hydrogen transfer from alcohols (18), glycerolysis of fats for the manufacture of monoglycerides (19), and alkylation of phenols by alcohols (20).

These reactions are usually considered to be base-catalyzed, and their reaction rates go through a maximum at a Mg/Al ratio of about 3 (13, 18, 20). From their catalytic properties hydrotalcites appeared more basic than MgO. It can be pointed out, however, that the rules governing the formation of basic sites are still unclear. On simple oxides basicity is determined in a first approximation by the electronegativity of the metal (21) and basic oxides are then those of electropositive metals. These oxides stored in air are usually carbonated and inert. Strong basicity appears only after high-temperature treatment to obtain the metal oxide surface (22–25). The strongly basic sites are identified with coordinatively unsaturated oxygen atoms formed by vacuum treatment or reduction at high temperature, typically >973 K on MgO (23–26). These centres can be considered as defects which exist in larger numbers on high surface area materials. This hypothesis accounts for the strong basic properties of clusters of magnesium or cesium oxide dispersed in zeolites by impregnation (27–29) and could also account for the basic properties of hydrotalcites, since the introduction of Al in the lattice of MgO induces a significant increase of the surface area. Indeed, the surface properties of spinels of the type  $Me(II)_xCr(III)_{2/3(1-x)}O$  with Me = Co, Ni, Cu, and Zn were explained by this model in which the

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surface was negatively charged while the positive charge was randomly distributed in the bulk (30, 31).

Our approach to the basicity of these solids was to investigate a series of double hydroxides containing Mg and either Al, Fe, and Cr as trivalent cations, or Al and Mg, Ni, Cu, and Zn as divalent cations. We attempted to obtain comparable surface areas of the mixed oxides to have similar dispersions, then a comparable number of defects, with solids composed of elements of different electronegativities. Most of the reactions reported above are bimolecular reactions, and previous work shows that these reactions often obey competitive mechanisms in which the reaction rate goes through a maximum for a certain ratio of the reactants (32). The reaction conditions are then critical in that case and the optimum conditions may not be the same for all samples. By contrast, monomolecular reactions involving a single adsorbed species are much simpler to analyse. We discovered incidentally that the isomerization of  $\beta$ -isophorone could be catalyzed by hydrotalcites and gave  $\alpha$ -isophorone. The thermodynamic equilibrium is completely displaced toward  $\alpha$ -isophorone at low temperature since the reverse reaction gives a low yield of 11%, even at 723 K (33). The acid-catalyzed isomerisation occurred as a competitive parallel reaction of the epoxidation by TBHP on titania-silica gels at 353 K (34): the conversion to  $\beta$ -isophorone of about 7% on pure Ti-SiO<sub>2</sub> fell to zero by the addition of small amounts of NaHCO<sub>3</sub> but increased to 95% by the addition of BaCO<sub>3</sub> and NaOH and 60% by that of MgO. Basic catalysis seems then faster than acid catalysis for this particular case and this simple model reaction was used to characterize basic solids.

## EXPERIMENTAL

### Preparation of Hydrotalcite Precursors

All LDHs were prepared by coprecipitation at 338 K and constant pH according to the experimental procedures described in detail in the literature (7–10). For the MgAl LDH, for instance, aqueous solutions containing the first one, 0.75 mol/L of MgCl<sub>2</sub> · 6H<sub>2</sub>O and 0.25 mol/L of AlCl<sub>3</sub> · 6H<sub>2</sub>O (for a ratio Mg/Al = 3), and the second one, 2 mol/L of NaOH and 0.5 mol/L of Na<sub>2</sub>CO<sub>3</sub>, were introduced into a 4-L flask by two electric pumps and mixed under vigorous stirring, maintaining a constant temperature of 338 K and constant pH of 9 ± 0.1. The mixture was aged at this temperature for 18 h with stirring. The precipitate was washed several times until the solution was free of chloride ions (AgNO<sub>3</sub> test) and then dried at 393 K. MgAl<sub>2.7</sub>(Cl<sup>-</sup>), MgFe<sub>1.80</sub>(NO<sub>3</sub><sup>-</sup>), ZnAl<sub>3</sub>(Cl<sup>-</sup>), NiAl<sub>2.23</sub>(NO<sub>3</sub><sup>-</sup>), and CoAl<sub>1.7</sub>(NO<sub>3</sub><sup>-</sup>) were prepared following this procedure using either chlorides or nitrates. The nomenclature of these solids indicates the  $M^{2+}/M^{3+}$  ratio and the nature of salt (Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>) used in the synthesis.

TABLE 1

Ideal Chemical Formulae of the Hydrotalcites, Usually Converted to the Carbonate Form, [(Cl<sup>-</sup>) and (NO<sub>3</sub><sup>-</sup>) Are for Chloride or Nitrate Precursor Salts]

Catalyst	Cell composition
MgAl <sub>2.7</sub> (Cl <sup>-</sup> )	Mg <sub>0.73</sub> Al <sub>0.27</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.13</sub> · 0.71H <sub>2</sub> O
MgAl <sub>2.98</sub> (NO <sub>3</sub> <sup>-</sup> )	Mg <sub>0.75</sub> Al <sub>0.25</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.12</sub> · 0.73H <sub>2</sub> O
MgCr <sub>3.13</sub> (Cl <sup>-</sup> ) <sup>a</sup>	Mg <sub>0.76</sub> Cr <sub>0.24</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.05</sub> Cl <sub>0.13</sub> · 1.2H <sub>2</sub> O
MgCr <sub>3.13</sub> (Cl <sup>-</sup> )	Mg <sub>0.76</sub> Cr <sub>0.24</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.120</sub> · 0.79H <sub>2</sub> O
MgCr <sub>2.8</sub> (Cl <sup>-</sup> )	Mg <sub>0.74</sub> Cr <sub>0.26</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.18</sub> · 0.83H <sub>2</sub> O
MgCr <sub>2.27</sub> (NO <sub>3</sub> <sup>-</sup> )	Mg <sub>0.7</sub> Cr <sub>0.3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.17</sub> · 0.84H <sub>2</sub> O
MgFe <sub>2</sub> (Cl <sup>-</sup> )	Mg <sub>0.67</sub> Fe <sub>0.33</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.16</sub> · 0.80H <sub>2</sub> O
MgFe <sub>1.66</sub> (NO <sub>3</sub> <sup>-</sup> )	Mg <sub>0.62</sub> Fe <sub>0.38</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.16</sub> · 0.84H <sub>2</sub> O
MgFe <sub>1.8</sub> (NO <sub>3</sub> <sup>-</sup> )	Mg <sub>0.64</sub> Fe <sub>0.36</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.14</sub> · 0.80H <sub>2</sub> O
MgFe <sub>2.21</sub> (Cl <sup>-</sup> )	Mg <sub>0.688</sub> Fe <sub>0.3112</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.16</sub> · 0.80H <sub>2</sub> O
ZnAl <sub>3</sub> (Cl <sup>-</sup> )	Zn <sub>0.75</sub> Al <sub>0.25</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.125</sub> · 0.84H <sub>2</sub> O
ZnAl <sub>2.74</sub> (Cl <sup>-</sup> )	Zn <sub>0.73</sub> Al <sub>0.27</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.14</sub> · 0.6H <sub>2</sub> O
ZnAl <sub>1.9</sub> (Cl <sup>-</sup> )	Zn <sub>0.65</sub> Al <sub>0.35</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.17</sub> · 0.6H <sub>2</sub> O
NiAl <sub>2.33</sub> (NO <sub>3</sub> <sup>-</sup> )	Ni <sub>0.70</sub> Al <sub>0.30</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.15</sub> · 1.2H <sub>2</sub> O
CoAl <sub>1.7</sub> (NO <sub>3</sub> <sup>-</sup> )	Co <sub>0.63</sub> Al <sub>0.37</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.18</sub> · 1.1H <sub>2</sub> O
CuAl <sub>3</sub> (NO <sub>3</sub> <sup>-</sup> ) <sup>a</sup>	Cu <sub>0.75</sub> Al <sub>0.25</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.42</sub> (NO <sub>3</sub> ) <sub>0.007</sub> · 1.41H <sub>2</sub> O
CuAl <sub>2.9</sub> (NO <sub>3</sub> <sup>-</sup> )	Cu <sub>0.74</sub> Al <sub>0.26</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.17</sub> · 1.2H <sub>2</sub> O

<sup>a</sup>Nonexchanged solid.

For MgCr<sub>3.13</sub>(Cl<sup>-</sup>) the pH for precipitation was 10 and the product was autoclaved for 8 days at 393 K, to increase the crystal size (34). For CuAl<sub>3</sub>(NO<sub>3</sub><sup>-</sup>) the conditions were pH 8 at 298 K.

The products of synthesis contained both Cl<sup>-</sup> (or NO<sub>3</sub><sup>-</sup>) and (CO<sub>3</sub><sup>2-</sup>) as charge-compensating anions, as established from the chemical analysis data reported in Table 1, taking into account the chemical analyses of the samples and the loss of water.

### Procedure of Anion Exchange

The exchange of Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> anions was performed by contacting the hydrotalcite with a solution of Na<sub>2</sub>CO<sub>3</sub>: 2 g of LDH was dispersed in 100 ml of a 0.2 M solution of sodium carbonate and stirred at 343 K for 2 h. After filtration, the solids were washed and dried at 313 K. To achieve a higher degree of exchange, a second exchange was sometimes carried out.

### Activation of the Catalysts

Catalysts (about 0.15 g) were first heated to 723 K in a flow of nitrogen, except CuAl, CoAl, and ZnAl, which were treated at 623 K. The temperature was raised 10 K/min to 723 K and maintained there for 8 h. The solid was then cooled in dry nitrogen.

In a few cases the mixed oxides were rehydrated to a LDH using the memory effect (9) of these systems. In that case the solid was first decarbonated as usual, then cooled to room temperature and contacted with a flow of nitrogen saturated with the vapor pressure of water for 12 h at this temperature.

The excess of water was removed by treating the sample under dry N<sub>2</sub> at 353 or 373 K. It has to be remarked that the memory effect is inoperative on MgCr samples.

### Characterizations

X-ray powder diffraction patterns were recorded on a Phillips instrument using CuK $\alpha$ <sub>1</sub> radiation. XPS measurements were performed on a spectrometer using AlK $\alpha$  radiation at 1486.6 eV. The integrated areas of the lines corresponding to Mg(1s) (binding energy: 1303.2 eV), Fe(2p<sub>3</sub>) (711.5 eV), Cr(2p<sub>3</sub>) (576.3 eV), and Al(2p) (73.8 eV) were compared, taking into account the factors of sensitivity of these elements. The kinetic energies corresponding to these transitions are rather different and correspond to different depths of analysis: superficial layers for Mg, but deep analysis for Al if we take into account the small size of the crystals after heat treatment. However, even if this analysis is not really restricted to the surface, it permits useful comparisons about the effect of heat treatment on the surface composition. The reference for the energies was C(1s) = 284.6 eV.

The textural analysis was performed on a home-made volumetric system, driven by a computer. The isotherm for N<sub>2</sub> adsorption at 77 K was determined on solids activated at 723 K in nitrogen or air and then desorbed *in situ* at 473 K in vacuum. DTA and TGA analyses were carried out in a Setaram TG-DTA 92 instrument operated under a flow of dry nitrogen at a heating rate of 5 K/min. The use of nitrogen permitted us to avoid the oxidation of Cr<sup>3+</sup> cations and the subsequent destruction of the structure reported in air.

The adsorption of CO<sub>2</sub> was followed by calorimetry using a Tian Calvet instrument and measurements of uptake using the experimental apparatus described in the literature (35). After treatment for 5 h in a flow of nitrogen at 723 K, reached with a temperature ramp of 10 K/min, the solid was transferred to the calorimetric cell under argon using a glovebag and then outgassed at 673 K until a good vacuum (10<sup>-4</sup> Pa) was reached. CO<sub>2</sub> was introduced in small increments at room temperature and the isotherm of adsorption was determined up to 133 Pa on a volumetric system equipped with a Baratron capacitance manometer for precision measurements. A trap containing the mixture CO<sub>2</sub>-acetone permitted us to dry the adsorbate. CuAl and ZnAl samples, which decompose at lower temperatures, were treated at 623 K.

In the case of the rehydrated samples, rehydration was performed in the flow reactor and then the temperature was slowly increased up to 373 K and maintained for 1 h to obtain a hydrated surface with no excess of water. The sample was then transferred to the calorimetric cell as usual.

### Catalytic Measurements

The kinetics of the isomerization of  $\beta$ -isophorone was followed in a three-necked 50-ml round-bottomed flask which

was heated at 308 K in an oil bath and equipped with a magnetic stirrer. Five milliliter of isophorone (Roche) was introduced with 30 ml of heptane as the solvent. The reactor was swept with a small flow of nitrogen to remove CO<sub>2</sub> from the atmosphere and stirred at 1000 rpm. When the thermal equilibrium was reached, the catalyst (0.15 g), freshly activated at 723 K (or 623 K for CuAl and ZnAl), was introduced and the progress of the reaction was followed by gas chromatography using a DB5 column.

## RESULTS

### Characterization of the Original Hydrotalcite Samples

The chemical compositions of the different solids are reported in Table 1. The XRD spectra shown in Fig. 1a demonstrate that the original samples are pure hydrotalcites. It is well known (5, 9, 36) that LDH can be obtained only in a limited range of composition, corresponding in the case of the MgAl sample to 0.2 < Al/Mg + Al < 0.33. Outside this range, the material is indeed a mixture of LDH and gibbsite or hydromagnesite. Since hydrotalcite corresponds to a solution of Al atoms in the lattice of brucite, the solid solutions thus obtained show lattice parameters following Vegard's law. The observation of this law ensures that the original MgAl samples are real solid solutions and was indeed obtained on the samples used here.

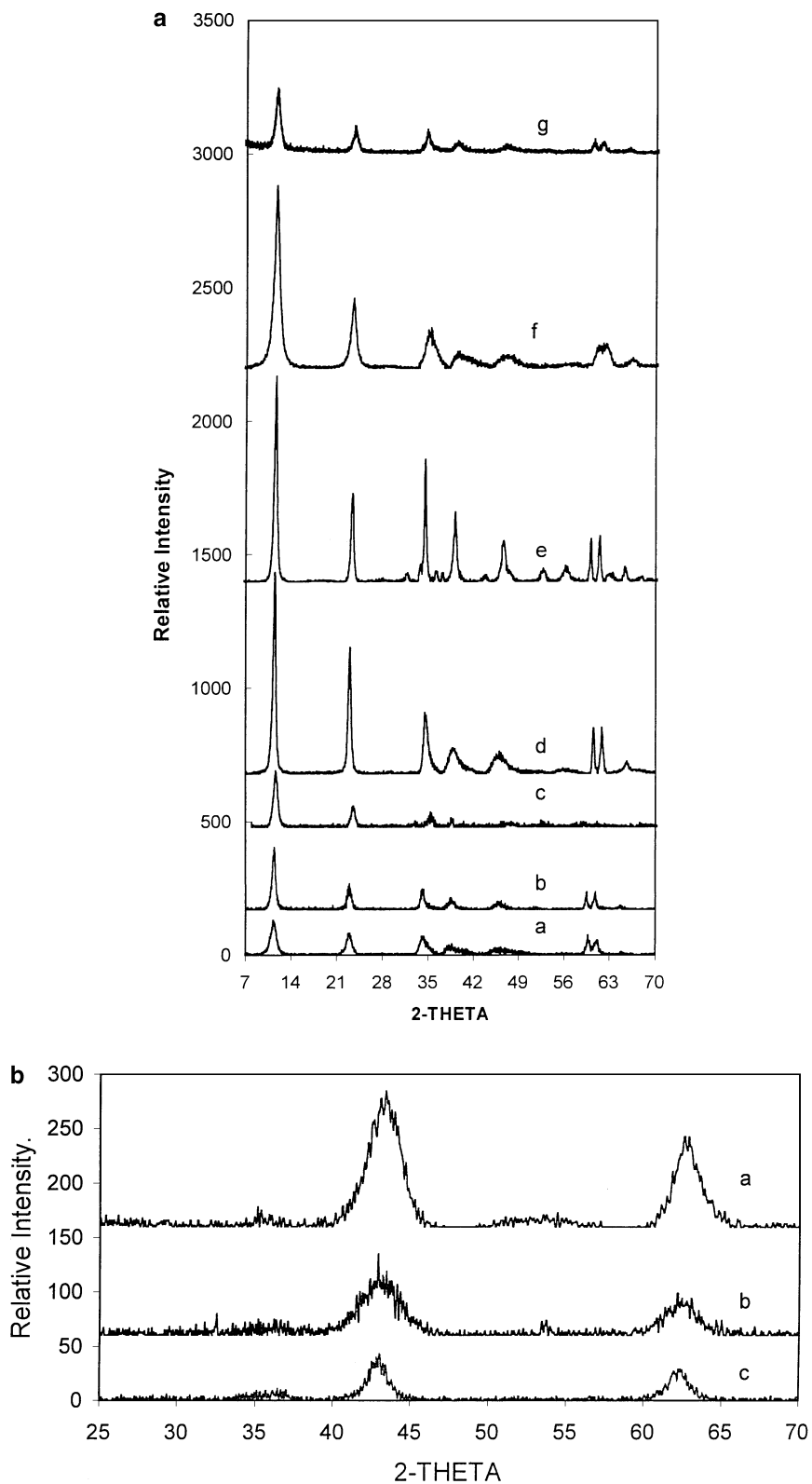
The size of the crystals was determined from the XRD patterns for the series of MgX (X = Al, Fe, Cr) LDH prepared from different salts and the results are reported in Table 2. The nature of the precursors appeared to have only a limited effect on the size of the crystals except in the case of MgCr, where the use of chlorides led to significantly smaller crystals.

Miyata first reported that these solids could be dehydrated to mixed oxides of an MgO structure which can be reversibly rehydrated to the layered structure (36). The XRD patterns of the MgX mixed oxides are reported in

TABLE 2

Size of the Crystals in Different Directions for Different LDHs, and for the Corresponding Mixed Oxides as Determined from XRD Patterns

Sample	Original samples		Heat-treated L(200) Å
	L(003) Å	L(110) Å	
MgAl2.7(Cl)	154	256	38
MgAl2.98(NO <sub>3</sub> )	183	214	
MgCr2.8Cl	68	232	35
MgCr(Cl)	40	79	
MgCr(NO <sub>3</sub> )	118	240	
MgFe(Cl)	120	246	71
MgFe(NO <sub>3</sub> )	100	234	



**FIG. 1.** a. XRD spectra of the original LDH materials: (a) MgCr<sub>2.8</sub>(Cl), (b) MgFe<sub>2</sub>(Cl); (c) CuAl<sub>2.9</sub>(NO<sub>3</sub>); (d) MgAl<sub>2.7</sub>(Cl); (e) ZnAl<sub>3</sub>(Cl); (f) NiAl<sub>2.33</sub>(NO<sub>3</sub>); (g) CoAl<sub>1.7</sub>(NO<sub>3</sub>). b. XRD spectra of the samples after activation at 723 K in nitrogen.

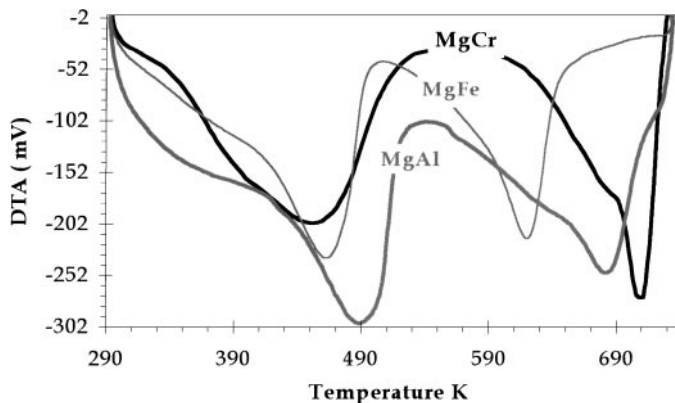


FIG. 2. DTA [traces of MgAl, MgFe, and MgCr] double hydroxides.

Fig. 1b. The size of the crystals of the cubic MgO solid solution computed from these patterns reported in Table 2 is not directly related to that of the parent LDH, since MgCr is close to MgAl after thermal treatment, but appears to be rather small which accounts for some of the difficulties in XPS analysis.

Decarbonation of hydrotalcites occurs at variable temperatures according to their composition. A typical thermogram is given in Fig. 2. The results of this measurement on the series of samples reported in Table 3 are in good agreement with those reported in the literature on similar samples. This temperature changed very little with the Mg/Al ratio but was more sensitive to the nature of cations and the Cl content. This poisoning effect of Cl was reported earlier for MgAl samples (37) and is of general value since it can be observed here, for instance, on MgCr<sub>3.13</sub>(Cl<sup>-</sup>): the sample in which Cl was exchanged by carbonates lost CO<sub>2</sub> at higher temperatures, i.e., was more basic. The average bonding energy of carbonates expressed by the temperature of decarbonation varies from 493 K for CoAl to 690 K for MgCr, therefore, in a rather large range.

TABLE 3

Results of the Thermal Analysis of Hydrotalcites of Different Compositions

Sample	Temp. water loss (K)	Loss of water (wt%)	Decarbonation temp. (K)	Rehydration wt% water
MgAl <sub>2.7</sub> (Cl <sup>-</sup> )	505	16.05	683	22.9
MgCr <sub>3.13</sub> (Cl <sup>-</sup> ) <sup>a</sup>	373	22.76	666	14
MgCr <sub>3.13</sub> (Cl <sup>-</sup> )	373–423	16.47	690	
MgFe <sub>2</sub> (Cl <sup>-</sup> )	455	15.67	614	11.1
ZnAl <sub>3</sub> (Cl <sup>-</sup> )			523	3.9
NiAl <sub>2.33</sub> (NO <sub>3</sub> <sup>-</sup> )	501	19.15	623	12.6
CoAl <sub>1.7</sub> (NO <sub>3</sub> <sup>-</sup> )			493	
CuAl <sub>3</sub> (NO <sub>3</sub> <sup>-</sup> ) <sup>a</sup>	353	18.2	523	

<sup>a</sup>Nonexchanged.

TABLE 4

Surface Area and Pore Radius of the Mixed Oxides Obtained by Decarbonation of Different LDH, and Evacuated at 473 K in Vacuum Prior to N<sub>2</sub> Adsorption

Sample	BET area (m <sup>2</sup> /g)	Pore radius (nm)
MgAl <sub>2.7</sub> (Cl <sup>-</sup> )	234	12
MgAl <sub>2.98</sub> (NO <sub>3</sub> <sup>-</sup> )	288	11
MgCr <sub>3.13</sub> (Cl <sup>-</sup> ) <sup>a</sup>	81	2–3
MgCr <sub>3.13</sub> (Cl <sup>-</sup> )	199	2
MgCr <sub>2.27</sub> (NO <sub>3</sub> <sup>-</sup> )	216	2–12
MgFe <sub>2</sub> (Cl <sup>-</sup> )	159	2–13
MgFe <sub>1.66</sub> (NO <sub>3</sub> <sup>-</sup> )	202	2–11
ZnAl <sub>3</sub> (Cl <sup>-</sup> )	51	2–12
NiAl <sub>2.33</sub> (NO <sub>3</sub> <sup>-</sup> )	260	2–5
CoAl <sub>1.7</sub> (NO <sub>3</sub> <sup>-</sup> )	153	5–12
CuAl <sub>3</sub> (NO <sub>3</sub> <sup>-</sup> ) <sup>a</sup>	119	2–12
CuAl <sub>2.9</sub> (NO <sub>3</sub> <sup>-</sup> )	56	2–12

<sup>a</sup>Nonexchanged solid.

Characterization of the Mixed Oxides

The calcination of hydrotalcites results in mesoporous mixed oxides of high surface area, even in the cases of Co oxides, which sinter easily when pure and are obtained here with areas of 150 m<sup>2</sup>/g after calcination at 623 K when stabilised by Al (Table 4). In all cases the XRD pattern is that of the divalent oxide amorphous matrix, as reported by many authors (5, 7, 9). The spinel structure appears only after calcination at higher temperatures.

Since these mixed oxides can be reversibly rehydrated to the layered structure after exposure to water vapor, it can be admitted that no large segregation occurs in the calcination step (3). The surface composition was measured by XPS on the Mg-based samples, either fresh or decarbonated at 723 K, and the resulting compositions are reported in Table 5. Remember that only the variations of the Mg/M<sup>β+</sup> ratio are significant. Except for MgFe (Cl), the Mg/M<sup>β+</sup>

TABLE 5

Surface and Bulk Compositions of MgFe, MgCr, and MgAl Samples after Pretreatment in Nitrogen at 723 K (Bulk Composition from Chemical Analysis and Surface Composition from the Intensities of Mg(1s)/M(2p<sub>3</sub>) XPS Lines for the Samples Containing Mg and Ni(3s)/Al(2s) for NiAl LDH

Sample	Chem. analysis	Ratio Mg/M <sup>β+</sup> from XPS		Binding energy O(1s) (eV)	
		Fresh sample	Treated 773 K	Fresh	Calcined
MgFe(NO <sub>3</sub> )	1.66	3.17	2.37	530.8	529.8
MgFe(Cl)	2.21	4.5	1.61	530.8	529.9
MgCr(Cl)	3.13	4.32	2.27	531.2	530
MgCr(NO <sub>3</sub> )	2.27	3.65	1.94	531.0	529.7
MgAl(Cl)	2.7	3.87	3.67	531.3	530.7

ratio showed only small changes upon calcination, and these changes corresponded systematically to a small increase of the concentration of the trivalent cation. The surface segregation has only very limited importance for MgAl samples and may be more significant for calcined MgFe and MgCr. The binding energies of the O(1s) lines is also reported in Table 5. These O(1s) lines were shifted by about 1 eV after calcination of the sample, suggesting a higher negative charge on oxygen. The line on the calcined samples was, however, usually asymmetric and composed of two lines except in the case of MgAl, which showed only a small asymmetry, attributed to a charge effect. The presence of the second line on the side of higher energies is evidence of a second oxygen species which was either in a second phase (surface segregation of  $M^{3+}$  oxide) or due to OH species or carbonates retained at the surface.

The mixed oxides showed an  $N_2$  adsorption isotherm (Fig. 3) of type IV in the classification of IUPAC, characteristic of a mesoporous solid. This is a favourable point for catalysis and adsorption since diffusional limitations are restricted.

#### Surface Properties of the Mixed Oxides

The surface properties of these mixed oxides were obtained from calorimetric measurements of the heat of adsorption of carbon dioxide. It has to be pointed out that while the samples first exchanged to the carbonate form adsorbed significant amounts of  $CO_2$ , the samples made from chlorides and not exchanged by carbonates adsorbed negligible amounts of  $CO_2$  and appeared then as inert. The type of residual anions at the surface is then important as reported before (37). From calorimetric measurements both the isotherms and the differential enthalpies of adsorption were obtained. The isotherms are reported in Fig. 4 and the enthalpies of adsorption in Fig. 5 for the different solids prepared by dehydration of the LDH.

Rehydration of the mixed oxides reformed the LDH structure, as expected from the literature (7, 9), except in the case of MgCr, which retained the MgO XRD pattern

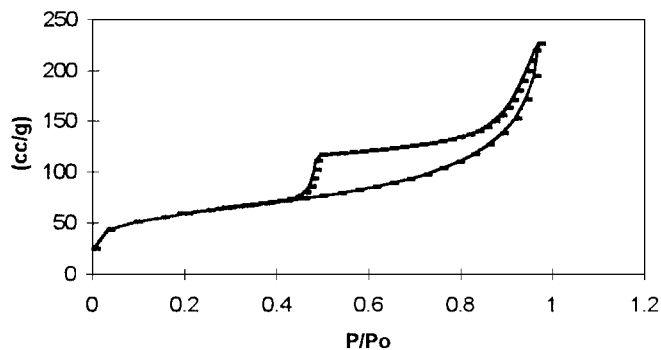
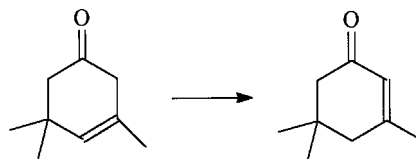


FIG. 3. Isotherm of adsorption-desorption of nitrogen at 77 K for MgAl<sub>2.7</sub> layered double hydroxides.



SCHEME 1

even after treatment in liquid water. Here, rehydration was performed in the gas phase to rehydroxylate the surface and avoid introducing water in the interlayer space since the loss of this water would perturb the calorimetric experiments. Indeed, the amount of water adsorbed in this process (Table 3) was lower than that required to completely rehydroxylate the sample. From XRD it appeared that the process was limited by the diffusion of water within the particles: if the LDH is visible in the X-ray pattern after 15 h with relatively broad lines, a better crystallinity, comparable to that of the original sample, requires about 2 days at room temperature in the case of an MgAl sample.

The adsorption of carbon dioxide on these hydrated solids is reported in Fig. 6. Rehydration induces a severe loss of surface area, and the amounts of  $CO_2$  adsorbed are reported here per gram of solid.

#### Catalytic Properties

The catalytic properties were determined for the isomerisation of  $\beta$ -isophorone to  $\alpha$ -isophorone (Scheme 1) on a series of samples prepared from chlorides. The solids were used in the dehydrated form which could be reproduced more safely for all samples. The only product of the reaction was  $\alpha$ -isophorone and the reaction was zero-order relative to the substrate. In that case the rate equation was reduced to  $r = k$ , and the initial rate was equal to the rate constant. The rate constant for isophorone isomerization is proportional, within experimental error, to the number of sites, as illustrated in Fig. 7. The only exception was MgCr, which was difficult to activate reproducibly and showed lower activity.

## DISCUSSION

The original samples appeared as pure LDH, i.e., a carbonated mixed hydroxide of low surface area, about  $50 \text{ m}^2/\text{g}$ , with similar crystal sizes for all samples, as determined from XRD line broadening (Table 2). Assuming that the temperature of decarbonation is representative of the average bonding energy of carbonates at the surface of the solid, it is possible to measure their basic properties by thermal analysis. The thermograms showed in all cases two weight losses which have been assigned to the removal of the interlayer water for the one between 450 and 520 K to the elimination of the structural water and carbonate species for the second (3, 4, 36, 39).

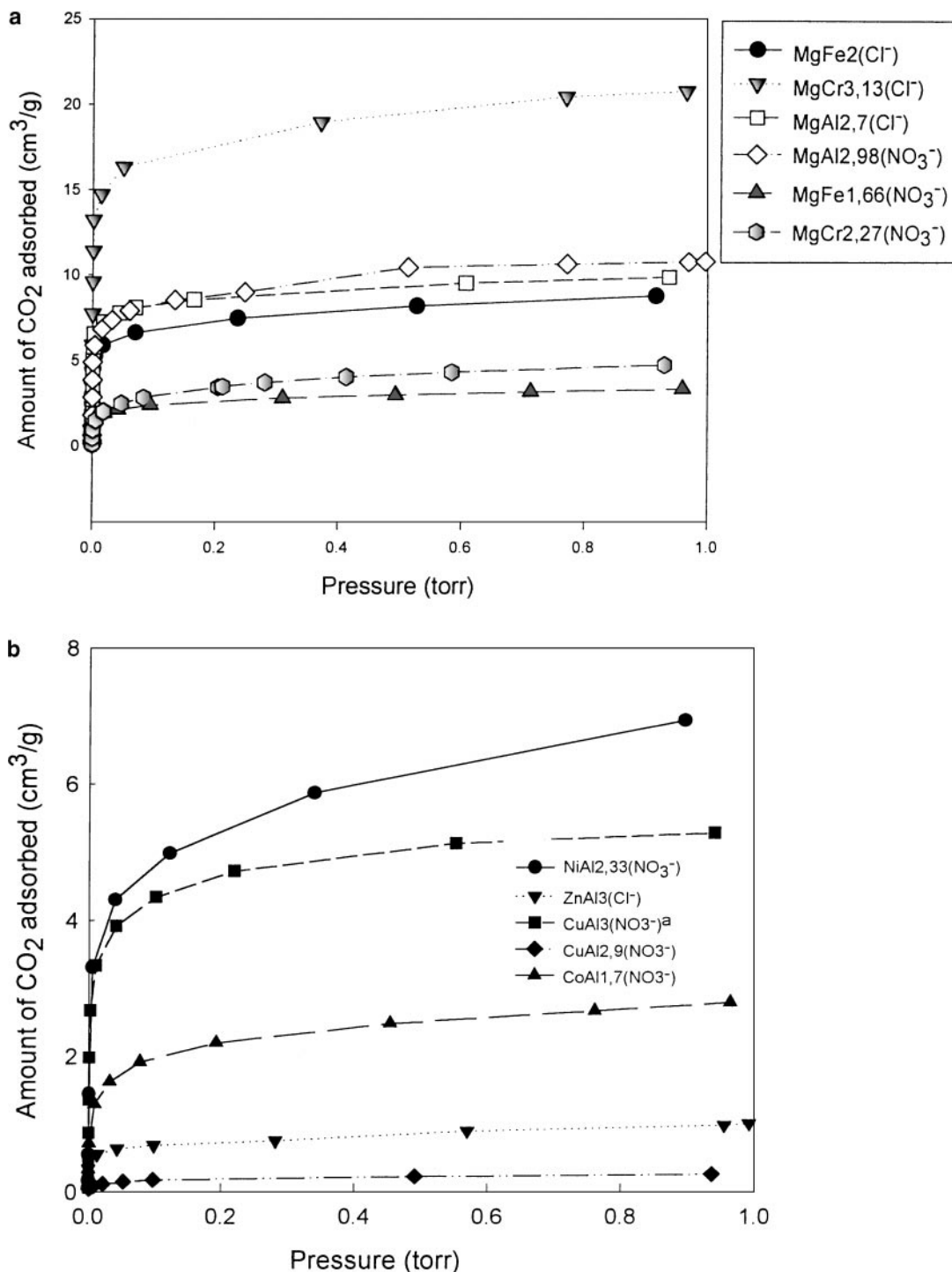


FIG. 4. (a and b) Adsorption isotherms of CO<sub>2</sub> on calcined layered double hydroxides prepared from different cations.

After carbonate exchange, the second peak ended at a higher temperature, showing that some carbonate species are more tightly bonded. Anion exchange resulted indeed in the elimination of chloride anions blocking the most basic sites. This effect is in agreement with the low basicity of Cl-containing samples observed in aldolisation (13, 14, 37)

or here in CO<sub>2</sub> adsorption. The effect was not linear since only a few ppm of Cl were retained, and it was previously proposed that these Cl anions exerted a long range influence on the basicity of the neighbouring OH, comparable to the influence of the last Na<sup>+</sup> cations on the acid strength of zeolites.

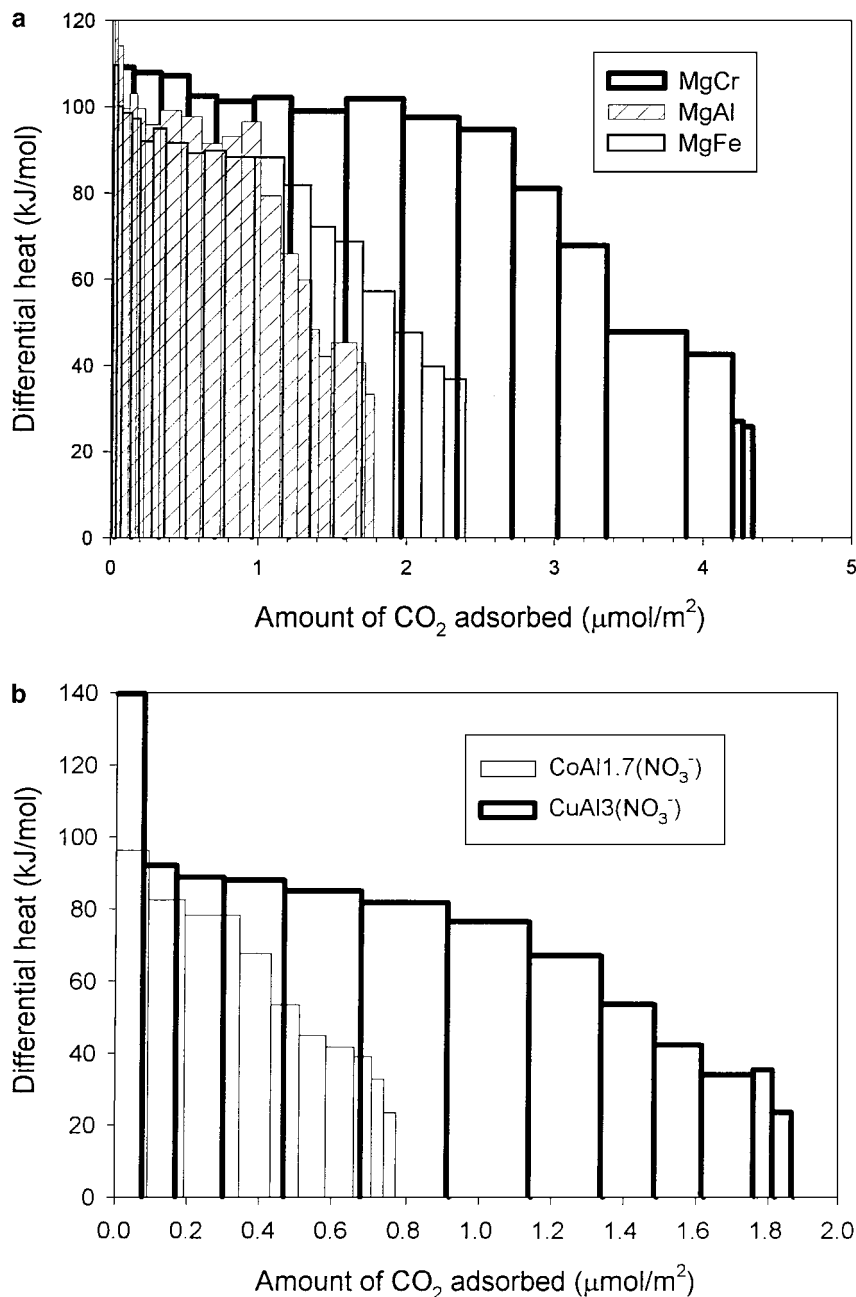


FIG. 5. Differential enthalpy of adsorption as a function of coverage for the adsorption of CO<sub>2</sub> on the mixed oxides obtained by decomposition on layered double hydroxides.

The position of the second peak is commonly related to the bonding energy of carbonates and can be related to the properties of the elements, for instance, the average charge on the oxygens. This can be calculated from Sanderson's theory of electronegativity (40, 41) or determined by XPS. According to this model, the intermediate electronegativity  $\chi$  of a compound is defined as a geometrical mean of the atomic electronegativities of the components. The average charge on an element can then be defined as

$$\delta i = (\chi - \chi_i) / \eta_i,$$

where  $\chi_i$  and  $\eta_i$  are the electronegativity and hardness of the element  $i$  under consideration. It is expected that the basic sites are the oxygen anions of the solid, and this model permitted us to compute the average charge borne by oxygen, knowing the chemical composition. The calculation was done using the electronegativity values of Allred and Rochow (42) and assuming that CO<sub>2</sub> desorbs from an LDH



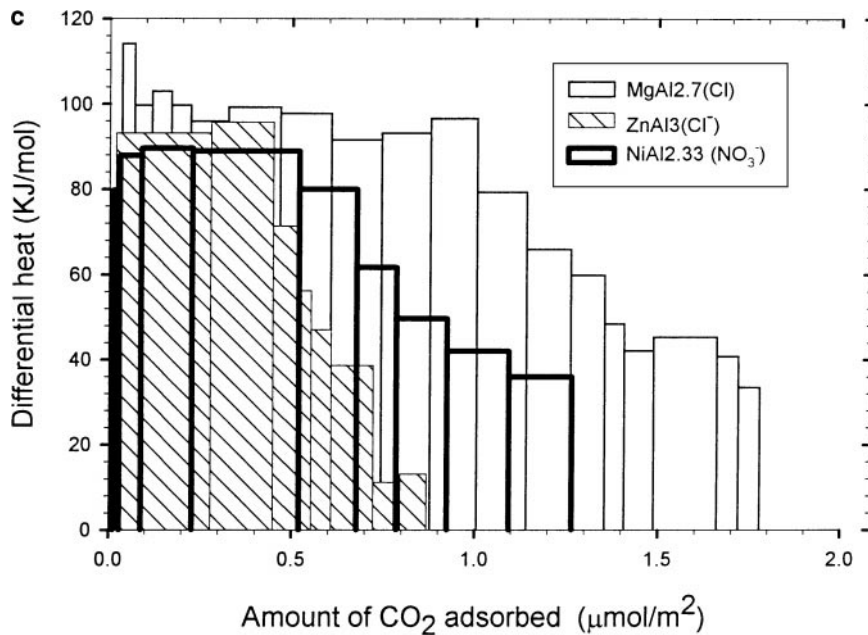
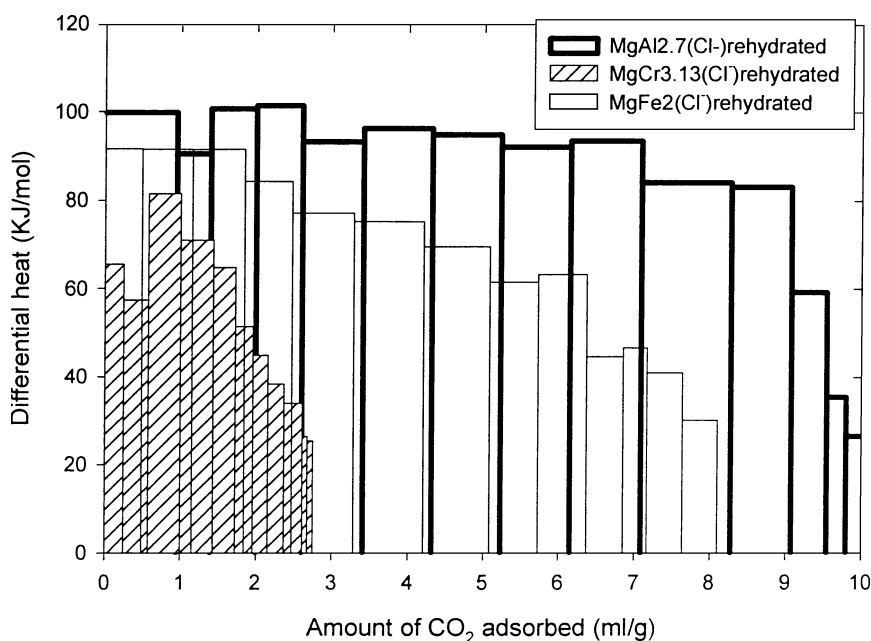


FIG. 5—Continued

of the composition reported in Table 1, in which OH simply replaces carbonates. A linear correlation can be obtained between the temperature of decarbonation (Table 3) and the partial charge of oxygen (Fig. 8). The only point which falls out of the correlation is NiAl; thus, in a first approximation, the basic properties of hydrotalcites are controlled by the electronegativity of the components. Basicity also changes with the chemical composition; however, the

$M^{2+}/M^{3+}$  ratio in hydrotalcites can be changed in a small range only, so that the effect of this ratio is relatively small. Small variations of the decarbonation temperature were reported earlier when the Mg/Al ratio was changed (37).

When we consider the series of trivalent cations in a Mg(OH)<sub>2</sub> matrix, the fresh samples show O(1s) energies which are indeed correlated with the average charge on oxygen calculated from the Sanderson model. As in alkaline

FIG. 6. Differential heat of adsorption as a function of coverage for the adsorption of CO<sub>2</sub> on rehydrated mixed oxides.

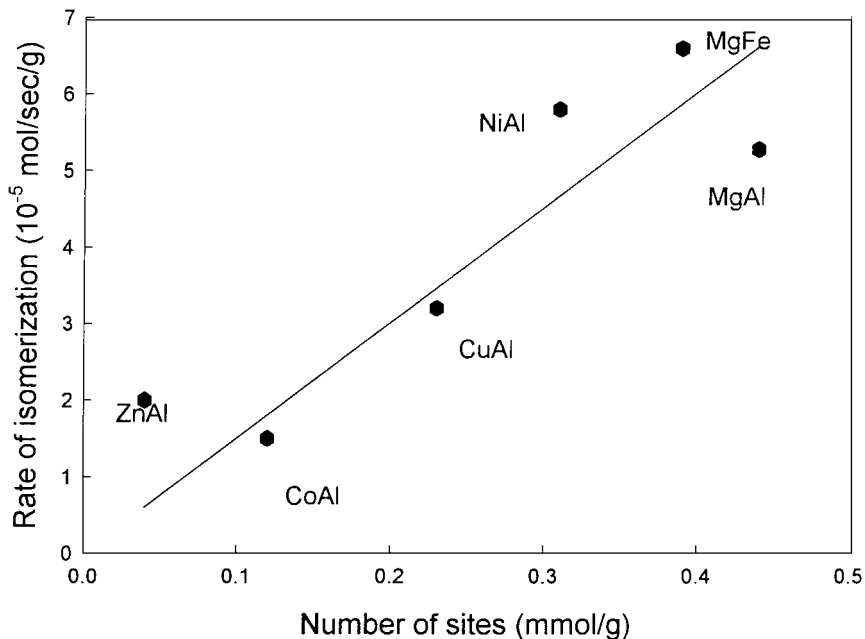


FIG. 7. Relationship between the rate constant for isophorone isomerization and number of sites for  $\text{CO}_2$  adsorption for layered double hydroxides activated in similar conditions in the two experiments.

zeolites, the  $\text{O}(1s)$  binding energy is related to the electronegativity of the cations and the average charge on oxygen. In that case a shift of about 0.7 eV in the  $\text{O}(1s)$  binding energy has been reported between  $\text{CsX}$  and  $\text{LiX}$  zeolites (43, 44). Here, the difference is smaller since the binding energy changes by about 0.5 eV between  $\text{MgFe}$  and  $\text{MgAl}$ . Upon decarbonation a shift by about 1 eV to lower energy is noticed for all LDH, and a difference by 0.9 eV is observed between  $\text{MgFe}$  and  $\text{MgAl}$  calcined LDH. XPS then suggests a higher basic strength for the decarbonated material and some differences between the mixed oxides. However, the partial hydrolysis of the lattice with surface enrichment in trivalent oxide reported above introduces a high complexity at the surface.

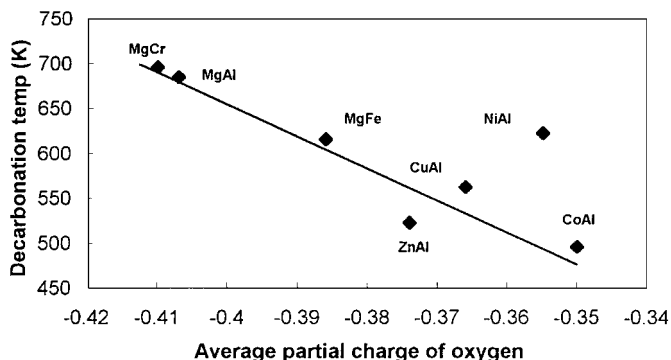


FIG. 8. Effect of the partial charge on oxygen, calculated according to Sanderson, on the bonding energy of carbon dioxide on layered double hydroxides of different compositions.

After heat treatment at 723 K the solid is converted to a partially hydrated mixed oxide. The adsorption of carbon dioxide followed by microcalorimetry gives a detailed picture of the surface properties of these mixed oxides. The isotherms of adsorption are of a Langmuir type on  $\text{MgAl}$  LDH, thus suggesting a relatively energetic homogeneity of the surface. The occurrence of a certain homogeneity of the surface for  $\text{CO}_2$  adsorption is confirmed by the plot of the differential enthalpies of adsorption versus coverage: an initial plateau of varying length did appear. It has to be pointed out, however, that several samples prepared from nitrates, such as  $\text{MgCr}$ ,  $\text{NiAl}$ , and  $\text{CoAl}$ , showed different behaviour with a much greater heterogeneity, as judged from the enthalpies of adsorption, and isotherms which follow better the Freundlich equation.

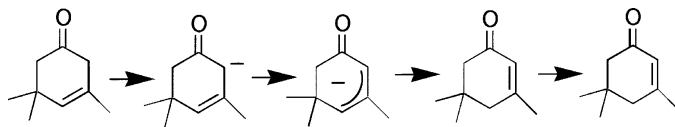
The enthalpy of adsorption at the plateau was 110 kJ/mol in all cases, i.e., close to the value reported by Auroux and Gervasini (45) for a  $\text{MgO}$  sample of about  $200 \text{ m}^2/\text{g}$  of surface area. The main difference between pure  $\text{MgO}$  and the mixed oxides resides in the number of sites: on pure  $\text{MgO}$  only a small fraction of sites, about  $0.6 \mu\text{mol}/\text{m}^2$ , adsorbed  $\text{CO}_2$  with an enthalpy of 110 kJ/mol. After this coverage a steep decrease of the heat was observed. By contrast, on the mixed oxides obtained from hydrotalcites the number of sites increased to nearly  $3 \mu\text{mol}/\text{m}^2$  adsorbing  $\text{CO}_2$  with the same high enthalpy.

The basic properties of the divalent oxides are not well documented with the notable exception of  $\text{MgO}$ . It appears here that bases stronger or comparable to magnesium oxide can be obtained by the decomposition of many double

hydroxides. The differential enthalpy of adsorption of CO<sub>2</sub> at low coverage is constant within experimental error on the series of mixed oxides, and the main variation concerns the number of sites, which is significantly altered by the change of the components. Indeed, the number of sites is related to the nature of the cations in the solid and corresponds to  $\frac{1}{6}$  of the total trivalent atoms in MgAl HDT,  $\frac{1}{4}$  in MgCr, and  $\frac{1}{8}$  in MgFe with close surface areas of  $210 \pm 20$  m<sup>2</sup>/g. For NiAl the number of sites per Al atom is  $\frac{1}{10}$  for a higher surface area of 260 m<sup>2</sup>/g. As was discussed above, some self-steaming occurs in the step of activation, and the trivalent cation segregates at the surface. Since these trivalent cations are acidic, they are expected to inhibit the stronger basic sites at the surface. This could account for the small differences found on the enthalpies of adsorption at low coverage.

Calcined hydroxalicates are only partially hydroxylated, and full rehydroxylation can restore the layered structure, with OH<sup>-</sup> as compensating anions. The surface properties of these rehydrated samples differ according to the conditions of evacuation after hydration: for a MgAl sample evacuation at 353 K results in a lower CO<sub>2</sub> uptake than evacuation at 373 K; water poisons the stronger sites. After evacuation at 373 K, thermogravimetric analysis shows that only some interlayer water is lost, and the surface remains then highly hydroxylated. This hydrated surface adsorbs CO<sub>2</sub> with the same high energy as the mixed oxide and small differences then appear between the heats of adsorption on MgAl and MgFe but MgCr, which was the most basic solid after vacuum treatment is then much weaker. The number of sites adsorbing CO<sub>2</sub> can be compared in Figs. 5 and 6: rehydration does not significantly change the number of sites for MgAl or MgFe samples but decreases the number of sites of MgCr by a factor close to 6. Remember that MgCr in liquid water could not be rehydrated to the LDH. MgCr NO<sub>3</sub> with large crystals, activated in nitrogen but not rehydrated, shows a low CO<sub>2</sub> adsorption (Fig. 4a) and a tendency to surface enrichment in Cr<sub>2</sub>O<sub>3</sub> (Table 4). This is an indication that self-steaming due to diffusional limitations on the desorption of water can occur when the crystals are large, and it can be supposed therefore that in both cases a partial destruction of the structure, which could account for a lower number of basic sites, occurs when the sample is treated with water at about 373 K or above. A similar partial decomposition of the structure upon rehydration in liquid water has been reported recently for Zn-Al LDH of lower basicity: from XRD, the Zn/Al ratio of the resulting LDH was close to 2, irrespective of the composition of the starting material (46).

From the point of view of enthalpies of adsorption of CO<sub>2</sub>, no large differences are noticed between the mixed oxide and the mixed hydroxide. Both solids appear as relatively homogeneous from the point of view of energetics when the structure is preserved. These two observations



SCHEME 2

suggest that the basicity of lattice oxygens (Lewis sites) and of hydroxyles (Brønsted sites) are similar, at least toward a relatively strong acid such as carbon dioxide.

The basic properties of the dehydrated samples were also investigated using the kinetics of  $\beta$ -isophorone isomerization as a tool of surface analysis. This reaction can be described as in Scheme 2: the formation of a carbanion by loss of a hydrogen which is labilised in the vicinity of an oxygen and of the double bond. The allylic carbanion can then isomerise to a species corresponding to the carbanion of  $\alpha$ -isophorone, which is stabilized by conjugation.

Since this reaction is zero-order with respect to the substrate, the initial rate is equal to the rate constant. These measures of activity can be compared to the number of sites determined by CO<sub>2</sub> adsorption, as illustrated in Fig. 7. A linear correlation is observed in which only MgCr falls apart, which can be attributed to some decomposition of this material during activation. It can then be concluded that both techniques are relative to the surface properties of the materials. CO<sub>2</sub> adsorption is then really restricted to the surface, as suggested earlier on the basis of the parameters of the infrared spectrum of adsorbed CO<sub>2</sub> (37).

In conclusion, LDHs are interesting model systems for the investigation of the basicity of solids. The good agreement on the number of sites determined by CO<sub>2</sub> adsorption and the results of a base-catalysed reaction is satisfactory since it justifies this technique for basicity characterizations. It can be concluded that, in the case of these double hydroxides activated at relatively low temperatures, in which the number of defects is low, basicity is governed not by the presence of defects which would readily react with water but by the differences of electronegativity between the cations and the components of the matrix. Defects can however be important for simple oxides activated at high temperatures: for instance, MgO activated at 1023 K and MgAl LDH activated at 723 K showed comparable activities for the base-catalyzed reaction of cyanoethylation of alcohols (47). An analogy can be made with solid acids: strong Lewis sites are formed on alumina by dehydroxylation above 873 K, in which case Al<sup>3+</sup> cations are exposed, but the formation of acid sites of zeolites is usually ascribed to the substitution of Si<sup>4+</sup> by M<sup>β+</sup> cations in the lattice of silicates.

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