Articles

Catalytic Properties of Layered Double Hydroxides and Their Calcined Derivatives

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Studies on the effect of the structural and compositional properties of layered double hydroxides (LDHs) and their decomposition products on the ethanolysis of propylene oxide to form glycol ethers are reported. The reaction, supported by results of indicator titrations, is used as a tool for elucidating the identity of the active sites in these materials. For LDHs, the catalytic behavior relates to their structural properties and the active sites can therefore be rationalized. In the case of their calcined derivatives, however, there is no apparent correlation due to the diversity of the active sites.

Introduction

Extensive research has been carried out to establish the correlation between the catalytic activity and selectivity for the solid acid catalysts comprising principally cationic clays and zeolites and their physicochemical properties.[1−4] Similar information has been obtained for base catalysts such as alkaline hydroxides,[5,6] carbonates[7] and oxides.[8,9] However, relatively little is known about potential bifunctional ones such as layered double hydroxides (LDHs)[10] —an inexpensive, versatile, and renewable source of a range of solid catalysts.[11] LDHs have a range of properties and these can be attributed to their variable compositions.

LDHs can be represented by the general formula $[M^{2+}_{1−x}M^{3+}_x(OH)_2][A^{m−}_{x/m}\cdot nH_2O]$ or $[M^+_{1−x}M^{3+}_x(OH)_2]$-$[A^{m−}_{(2x+1)/m}\cdot nH_2O]$. M^+, M^{2+}, and M^{3+} are metal cations which are cross-linked through hydroxide groups to form a dimetal hydroxide sheet otherwise know as the cationic layer.[11] $A^{m−}$ denotes anions which together with "n" (the molecules of water), constitute the anionic layer. Due to the ability to vary these components and consequently their chemical properties, LDHs have attracted considerable interest across a wide range of fields including, predominantly, catalysis.

Catalysts generated from LDHs are employed in several industrial reactions such as polymerization,[12,13] condensation,[14−17] and alkylation.[18] To date, investigations on these reactions have centered around the exploitation of catalysts generated from calcining LDHs. These are characterized by uniformly dispersed metal atoms in a stable oxide matrix and have higher surface areas compared to their precursors. The claim that uncalcined LDHs are catalytically inactive[19] is discredited by the observations that have been made during the aldol condensation of acetaldehyde that the LDH-calcined derivatives reconstitute to LDHs without loss in catalytic activity.[17] The transformations have been attributed to the reaction between the water produced by the condensation process and the metal oxides.

The work presented in this paper was carried out to establish the nature of the active sites in an LDH before and after calcination. By analysis of the products from the ethanolysis of propylene oxide (a reaction which may be acid- or base-catalyzed) using selected LDHs and their calcined derivatives as catalysts, their acidic and basic properties could be determined unambiguously.

Experimental Section

Synthesis of Hydrotalcite-like LDHs. The samples were prepared from standard analytical grade chemicals supplied by Aldrich Chemical Co. Two solutions, one containing the metal salts in divalent to trivalent cation molar ratios of 3:1 or 2:1 and the other containing 0.6 mol of NaOH dissolved in 300 mL of decarbonated water, were added dropwise into a container while maintaining a constant pH. The pH

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Table 1. Properties of the Organic Indicators Used in the Titration

indicator	acid form	base form	pK_a
Crystal Violet	blue	yellow	0.8
Bromophenol Blue	yellow	blue	3.0; 4.6
Methyl Red	pink	yellow	4.2; 6.3
Bromothymol Blue	yellow	blue	6.0; 7.6
Phenol Red	yellow	red	6.8; 8.2
Phenolphthalein	colorless	red	8.0; 10.0
2,4,6-trinitroaniline	yellow	amber	12.2

values were similar to those used in the syntheses by Kuma *et al.*[20] In the preparation of LDHs containing carbonate anions (Ni–Al, Ni–Fe, Mg–Al, and Mg–Fe), 0.2 mol of Na_2CO_3 was added to the alkali solution before precipitation. The precipitated gels were aged at 65 ± 2 °C for 18 h followed by cooling, isolation of the solids by repeated filtering and washing, and, finally, drying at 105 °C overnight. The calcined samples were obtained by heating the dry LDHs at 450 °C for 14 h.

Synthesis of Oxometalate Anion LDHs. A 0.05 M solution (50 mL by volume) of the acid salt was added dropwise at room temperature to 50 g of terephthalate slurry while bubbling with N_2. Details of the preparation of a terephthalate slurry are reported elsewhere.[21] The addition took 45 min during which the pH dropped from 12.3 (pH of slurry) to 4.5 ± 0.5 (pH of the resultant mixture). The solids were obtained from their mixtures by filtration, repeated washing with hot decarbonated water, and then drying at 95 °C. The samples will be referred to as MAP-1 and MAS-1 for the preparations performed using $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively.

Characterization Methods. Powder X-ray diffraction (PXRD) data were obtained between 3 and 80 (2θ°) on a Philips 1710 powder diffractometer for samples deposited on glass slides using Cu Kα radiation (λ = 1.5418 Å) and a step size of 0.05° at a counting rate of a second per step.

N_2 adsorption measurements were carried out by the nitrogen BET adsorption method on a Micromeritics ASAP 2000 analyzer. The absorbents were removed from the sample surfaces by outgassing at 100 °C until a vacuum of the order of 10^{-6} Torr had been attained. Prior to this procedure (which lasted between 2 and 12 h), the volume above the sample was measured using helium gas.

Elemental compositions were determined using a Perkin–Elmer 380 atomic absorption spectrometer (for Mg and Al), Camscan S4 scanning electron microscope (for Si, W, and P), and a Carbon Hydrogen Nitrogen Carlo Erba 1106 elemental analyzer (for H).

Acidity and Basicity Measurements. A measure of the acid–base functionalities of a sample can be determined by visual inspection of the color of suitable indicators adsorbed on a surface.[22] The lower the pK_a the greater the solid's acid strength. For example, a solid which gives a blue coloration with bromothymol blue (pK_a strength between 6.0 and 7.6) and is colorless with phenolphthalein (pK_a strength between 8.0 and 10.0), has an acid strength H_o which lies between 6.0 and 10.0.

In view of the visual limitation inherent in determining surface acidity and basicity by indicator adsorption, titration measurements were limited to light colored samples. The analysis, using the indicators listed in Table 1, was as follows: 0.2 g of a finely powdered sample was placed in a 25 mL conical flask avoiding exposure to moisture as practically as possible. Then 2 mL of the indicator which had been dissolved in benzene or dichloromethane was added and the mixture shaken briefly. In some cases the transition between acidic and basic conditions was gradual and the end points could not be determined unambiguously. A cut of time of 10 min was chosen.

Catalytic Reaction. A mixture containing ethanol and propylene oxide in a volume ratio of 10 to 1 was mixed with 1 g of powdered sample in 25 mL stainless steel autoclaves. The vessels were heated to 120 ± 5 °C in a vacuum oven at autogenous pressures. To optimize the contact between the reactants and the catalyst, the autoclaves were shaken hourly for 30 s. They were removed after 5.5 h and cooled in

Table 2. Sample Identity from Powder X-ray Diffraction and Chemical Analysis

acronym	identity	JCPDS[a] file no.
ZA-1	Zn–Al nitrate LDH[23]	
ZA-2	$Al_2O_3\cdot ZnO$, ZnO[b]	5-664, 22-1034
LA-1	Li–Al chloride LDH[24]	
NF-1	Ni–Fe carbonate LDH[25]	
NF-2	$(Fe_{0.67}Ni_{0.33})OOH$[b]	14-556
NA-1	Ni–Al carbonate LDH[23]	
NA-2	$NiAl_2O_4$, NiO[b]	10-339, 4-835
MC-1	Mg–Cr nitrate LDH[23]	
MC-2	$MgCrO_4$[b]	22-1148
MA-1	Mg–Al carbonate LDH[26]	
MA-2	$MgAl_2O_4$[b]	33-853
ZC-1	Zn–Cr nitrate LDH[27]	
ZC-2	$Zn_2(OH)_2CrO_4$[b]	22-1107
MF-1	Mg–Fe carbonate LDH[25]	
MF-2	$MgFe_2O_4$[b]	17-46
MAP-1	$Mg_{0.3}Al_{0.13}(OH)_{0.61}(PW_{10}O_{39})_{0.014}$-$(WO_4)_{0.14}\cdot 0.51H_2O$[c]	
MAS-1	$Mg_{0.28}Al_{0.15}(OH)_{0.95}(SiW_{12}O_{40})_{0.015}\cdot$ $1.66H_2O$[c]	

^{a} JCPDS = Joint Committee on Powder Diffraction Standards files.
^{b} Refers to assignments based on JCPDS files or chemical analysis.
^{c} Refers to identity based on elemental analysis.

an ice bath prior to opening. The liquid products were obtained from the mixture by centrifugation, separated on a 25 meters long BP25–05 capillary column coated with polyethylene glycol, and identified by mass spectrometry.

Results and Discussion

Structural Properties. The compositions of the samples are presented in Table 2. These were identified using elemental analysis or by a comparison of their PXRD data with JCPDS tables of pure compounds, or by diffraction data from reported works.[23–27]

The presence of well defined 003 and 006 reflections in the diffractograms of MA-1, ZA-1, NA-1, and LA-1 (Figure 1) is consistent with ordering of the layers in the c-axis direction. The 00l reflections for NF-1, ZC-1, MC-1, MF-1, MAS-1, and MAP-1 (Figures 2 and 3) are broad and poorly defined compared to those of NA-1, ZA-1, LA-1, and MA-1, indicating the existence of structural disorder. The properties displayed by the polyoxometalate LDHs are due to turbostatic disorder caused by the high charge density of the anions.[28] For LDHs containing carbonate or nitrate anions, the arrangement of the layers is ordered[29] (hence the crystallinity of MA-1, ZA-1, NA-1, and LA-1). The broad features observed in the diffractograms of NF-1, MF-1, ZC-1, and MC-1 (these do not contain polyoxometalate anions) are due to defects arising from Cr^{3+} or Fe^{3+} sites. Comparable features are observed with all LDH-calcined derivatives. Two representative diffractograms are shown in Figure 4.

Since the product distribution from heterogeneous reactions is also influenced by sorption properties, the porosity of the samples was investigated. The surface characteristics (reported in Table 3) reveal that with the exception of ZA-1, ZA-2, and NF-2 (which are macroporous), LDHs and their calcined

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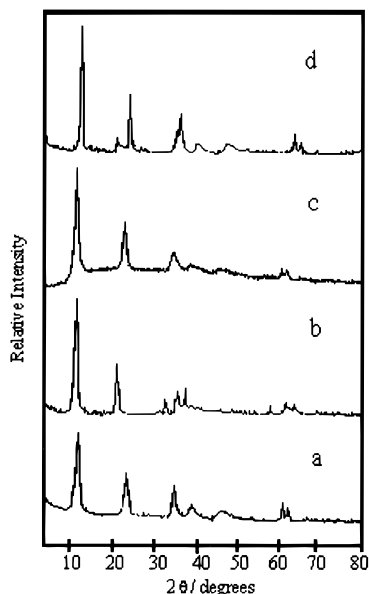(22) Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.

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Figure 1. X-ray diffraction patterns for (a) Mg−Al carbonate, (b) Zn−Al nitrate, (c) Ni−Al carbonate, and (d) Li−Al chloride LDHs.

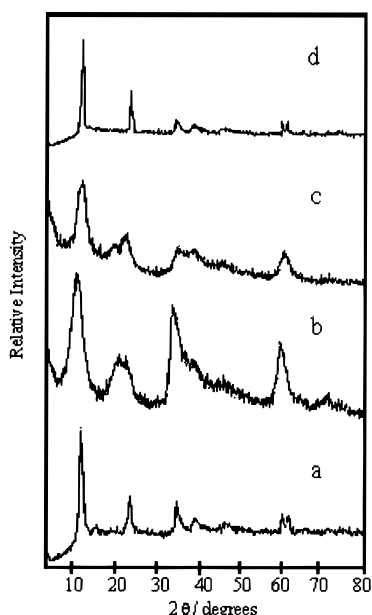**Figure 2.** X-ray diffraction patterns for (a) Ni−Fe carbonate, (b) Zn−Cr nitrate, (c) Mg−Cr nitrate, and (d) Mg−Fe carbonate LDHs.

Figure 3. X-ray diffraction patterns for (a) $Mg_{0.28}Al_{0.15}(OH)_{0.95}$-$(SiW_{12}O_{40})_{0.015} \cdot 1.66 \ H_2O$ and (b) $Mg_{0.30}Al_{0.13}(OH)_{0.61}(PW_{10}O_{39})_{0.014}$-$(WO_4)_{0.14} \cdot 0.51 \ H_2O$.

Figure 4. X-ray diffraction patterns of the calcined derivatives for (a) Zn−Cr nitrate and (b) Mg−Fe carbonate.

Table 3. Surface Characteristics of Layered Double Hydroxides and Their Calcined Derivatives

acronym[a]	surface area (m²/g)	micropore %	mesopore %	macropore %
ZA-1	21	0	13	87
ZA-2	38	0	7	93
NF-1	117	0	87	13
NF-2	133	0	12	88
MA-1	69	0	81	19
MA-2	232	4	94	2
MC-1	38	1	68	31
MC-2	139	1	73	26
ZC-2	50	0	99	1
MF-2	127	9	91	0
LA-1	115	0	86	14
NA-2	145	0	96	4

[a] The definition of acronyms is as indicated in Table 2.

Table 4. Acid−Base Values of Layered Double Hydroxides and Their Calcined Derivatives

acronym[a]	acidity−basicity range	acronym[a]	acidity−basicity range
MA-1	∼12.2	ZA-1	6.0−8.2
MA-2	8.2−12.2	ZA-2	6.0−10.0
LA-1	10−12.2	MAS-1	0.8−3.0
LA-2	10−12.2	MAP-1	0.8−3.0

[a] The definition of acronyms is as indicated in Table 2.

derivatives are largely mesoporous. These pores are the cracks and crevices between the sample platelets, and it is through them that the reacting species access the active sites and the resulting products migrate from. In view of the general similarity in the pore structure of the LDHs and their calcined derivatives and the lack of any correlation between porosity and catalytic properties (discussed below), it can be concluded that it is the identity of the active sites rather the overall pore structure that determines the catalytic potential of LDHs and their calcined derivatives.

Acidic and Basic Properties. Qualitative analysis of the color changes using the indicators revealed that the samples fall into three groups (Table 4): those with strong basicity ($pK_a > 8.2$), an intermediate group with pK_a values between 6 and 8.2, and a relatively acidic group with values below pK_a 6.

Included in the first category are MA-1 and LA-1. Although the identity of the anions in these samples differ, carbonate for MA-1 and chloride for LA-1, their basicities are comparable. This is in conformity with the rationalization that because the
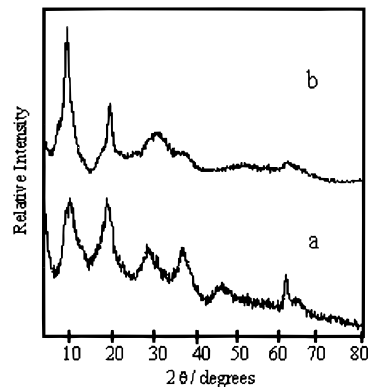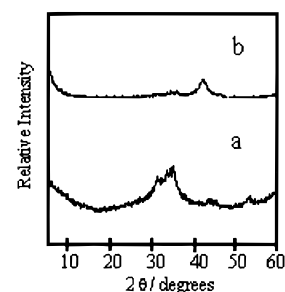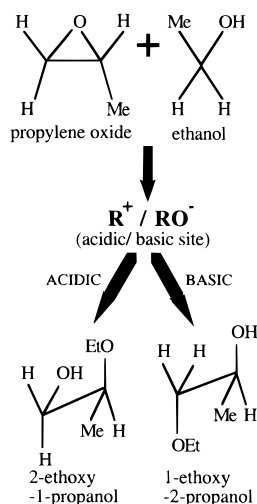
anions are located between cationic layers with which they charge balance, varying their identity has no effect on the acidity or basicity of a well-ordered LDH. This result is particularly significant as it corroborates the Cl⁻ grafting theory proposed in ref 10 which was used to explain the acidic property of a chloride LDH after thermal activation.

ZA-1 displays a much lower base strength than either MA-1 or LA-1. Since intercalated anions do not influence the acid−base properties of an LDH and the trivalent cation is the same in all three samples, it can be argued that the difference between

Scheme 1. Mechanism for the Formation of 1-Ethoxy-2-propanol and 2-Ethoxy-1-propanol

Table 5. Activity of Calcined and Uncalcined Layered Double Hydroxides in the Glycol Ether Reaction

acronym[a]	LDH conversion (%)		acronym[a]	LDH conversion (%)	
	uncalcined	calcined[b]		uncalcined	calcined[b]
MA-1	9	19	ZC-1	8	10
NF-1	11	25	NA-1	7	14
MC-1	10	11	MF-1	8	21
LA-1	7	11	MAS-1	13	n.s.[c]
ZA-1	9	7	MAP-1	12	n.s.[c]

[a] The definition of the acronyms is as indicated in Table 2. [b] The calcined samples were obtained by heating the dry LDHs at 450 °C for 14 h. [c] n.s. = not screened.
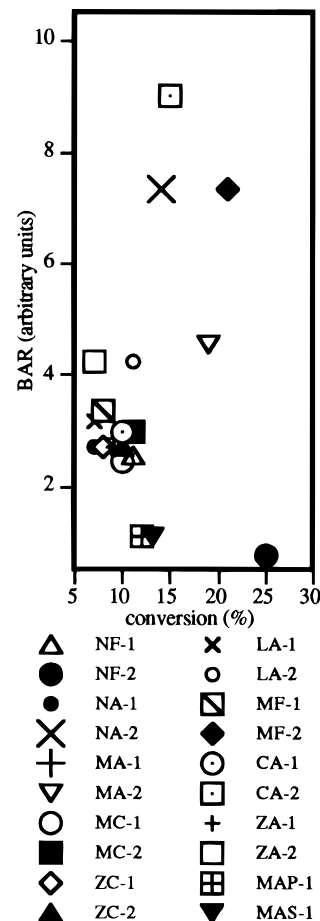

Figure 5. Basicity acidity ratio (BAR) *vs* conversion for layered double hydroxides and their calcined derivatives.

the basicity of ZA-1 and that of its analogues is due to the identity of the second cation—Zn^{2+} for ZA-1, Li^+ for LA-1, and Mg^{2+} for MA-1. The ionicities of Mg^{2+} and Li^+ and consequently the basicities are similar, whereas that of Zn^{2+} is an order of magnitude lower—hence the apparent acidity of ZA-1.

LDHs pillared with oxometalate anions along with their calcined derivatives display the highest acidity. Though the structure of the former is understood to consist of anions sandwiched in between cationic sheets,[28,30,31] the observed physicochemical properties suggest otherwise. Chemical analysis indicates that some polyoxometalate LDH samples contain products of anion hydrolysis. These are the source of the observed acidities since LDHs containing Mg and Al cations (exemplified by MA-1) are basic. The polyoxometalate species are not removed by the repeated washing performed during synthesis since they are chemisorbed on the LDH surface.

The calcined derivatives fall under the same basicity grouping as their precursors: LA-2 and MA-2 in the strongly basic and ZA-2 in the intermediate one. These samples consist of either dimetal oxides or oxide hydroxides—the former otherwise known as spinels. Studies on the structural properties of spinels using a combination of adsorption and spectroscopic techniques by Morterra *et al.*[32] and Busca *et al.*[33] have revealed that irrespective of the pre treatment temperature the spinels can not be devoid of hydroxyl groups. It is therefore not unusual to observe that even though an LDH's composition is significantly altered by the decomposition process, the acid-base properties are not.

Catalytic Properties. Scheme 1 shows the main products formed on the basic and acidic sites during the ethanolysis of propylene oxide. Ethoxy−propoxy−propanol isomers are also formed in minute quantities. The terms "conversion" and "selectivity" (for 1 g of catalyst) as used in the discussion are defined as follows:
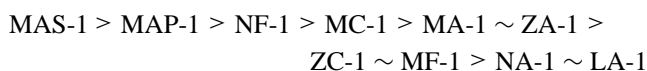
$$\text{conversion (\%)} = (A - B)/A \times 10^2 \quad (1)$$

$$\text{selectivity to 2-ethoxy-1-propanol (\%)} = C/(C + D) \times 10^2 \quad (2)$$

$$\text{selectivity to 1-ethoxy-2-propanol (\%)} = D/(C + D) \times 10^2 \quad (3)$$

where A and B are the mole fractions of both propylene oxide and ethanol in the feed and product respectively, and C and D those of 2-ethoxy-1-propanol and 1-ethoxy-2-propanol in the products.

Table 5 shows the calculated conversions for LDHs before and after calcination. The conversion trend for the LDHs is

$$\text{MAS-1} > \text{MAP-1} > \text{NF-1} > \text{MC-1} > \text{MA-1} \sim \text{ZA-1} >$$
$$\text{ZC-1} \sim \text{MF-1} > \text{NA-1} \sim \text{LA-1}$$

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The conversions parallel the acidity classification concluded from the Hammett indicator titration results—the highest values are obtained from the "highly acidic" group and the lowest from the "basic" one. In the intermediate group are MC-1 and NF-1 which like MAS-1 and MAP-1 have extensive structural deformities. Lattice and surface defects which have been generated during synthesis are also known to promote an oxide's catalytic activity.[34]

The conversion trend observed with the LDH calcined derivatives is

$$NF\text{-}2 > MF\text{-}2 > MA\text{-}2 > NA\text{-}2 > MC\text{-}2 \sim LA\text{-}2 >$$
$$ZC\text{-}2 > ZA\text{-}2$$
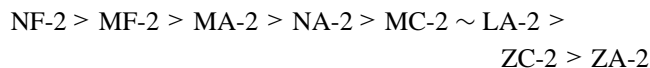
The samples consist of mixtures of spinels, mixed metal oxides, or single metal oxides (Table 2). The main feature of NF-2 (highest in the series) is the presence of hydroxide anion moieties which act as the active sites. In the case of ZA-2 (lowest conversion), the sample has been identified as comprising of a mixture of zinc aluminate and zinc oxide which exhibit an intermediate basicity. LA-2 compares with MA-2 in terms of base strength but displays a conversion closer to that of ZA-2. The conversions obtained using LDH-calcined derivatives do not relate to any active site type.

To compare the relative amounts of acid and base sites, the proportion of the basic product was normalised to that of the acidic one. A plot of the calculated values (hereafter referred to as BAR (short for basicity acidity ratio)) *vs* conversions is displayed in Figure 5. The ratio is used to derive qualitative information only in view of the fact that minor products are formed in the reaction. The plot reveals that the values of all the uncalcined LDHs fall within a one window unit with the exception of LDHs based on polyoxometalate species. Since the values for ZC-1, MC-1, and MF-1 do not differ significantly from those of their analogues (despite the presence of cation defects), it is concluded the catalytic properties of LDHs are largely influenced by one type of site—the hydroxide moieties.

In the case of the LDH-calcined derivatives (comprised largely of spinels), the BAR values do not relate to any active group type. Those with a Cr_2O_3-based component are close to the proportions obtained using corresponding LDH samples. On the other hand the aluminates have values which are higher than those of their precursors—double in the case of NA-2. For the Fe_2O_3-based samples, the BAR values are reduced when NF-1 is activated but doubled when MF-1 is. The lack of any correlation between product selectivity and structural properties underlines the diversity of the active site types in the calcined derivatives.

The selectivity to the base catalyzed product (1-ethoxy-2-propanol) displayed by most samples is an indication of their predominantly basic properties. Only with NF-2, MAS-1, and MAP-1 are equal proportions of the acid- and base-catalyzed products obtained. It is noteworthy that the deductions gleaned using the catalytic screening and the indicator methods complement each other despite the formation of a minor product in the former and the restriction with the latter to lightly colored samples.

Summary

This study demonstrates that LDHs do not have a purely basic character even after calcination. Some LDHs (for example those pillared with polyoxometalate anions) are strongly acidic. Though thermal activation of LDHs is a widely accepted practice, the observations made on the reaction demonstrate that LDHs possess some catalytic potential and could, therefore, be an alternative to the calcined derivative.

Considerable interest has been circumscribed to catalysis occurring primarily on the basic sites present in LDH-calcined derivatives although as illustrated by this study, their identity varies with the composition of the precursor. On the basis of the combined results from catalysis and titration methods, the active sites in parent LDHs are the hydroxide groups. In the case of LDHs containing polyoxometalate anions, the sites include anionic groups as well. For the calcined derivatives, the following three sites are present: O^{2-} centers which are directly linked to metal atoms (strong basicity), O^{2-} ions bonded to atoms adjacent to the metal centers (medium basicity), or surface OH groups (weak basicity).

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