Epoxydation of Activated Olefins by Solid Bases

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The epoxidations of 2-cyclohexen-1-one and β-isophorone by hydrogen peroxide and *tert*-butyl hydroperoxide have been investigated on basic catalysts including mild bases such as hydrotalcites activated in different conditions and fluorinated hydrotalcites, and two stronger bases, KF/Al$_2$O$_3$ and MgLa mixed oxides. The solids containing transition metal cations are unselective since they catalyze mainly the Fenton decomposition of H$_2$O$_2$ to O$_2$. MgAl hydrotalcites are active for the epoxidation with *tert*-butyl hydroperoxide after decarbonation and rehydration of the surface. The catalytic properties are roughly dependent on the basic strength of the solids, and MgLa mixed oxides decarbonated at 823 K shows a higher activity for the epoxidation of isophorone by hydrogen peroxide comparable to that of titanosilicates.   © 2002 Elsevier Science (USA)

Key Words: epoxidation of activated olefins; isophorone; basic catalysis; TBHP; hydrogen peroxide; MgLa mixed oxides; hydrotalcites; activation.

INTRODUCTION

The use of basic heterogenous catalysts is an area of growing interest since it was realized that it was far less developed than that of acid catalysis (1, 2). Due to the great importance of oxidation reactions in organic synthesis, the application in this field of solid basic catalysts is also a subject of current interest (3). Epoxidations of activated olefins by *tert*-butyl hydroperoxide (TBHP) or hydrogen peroxide have been performed mostly using Ti catalysts (4), but these reactions are also catalyzed by solid bases (5). In that case the mechanism is similar to that of the Michael reaction (6), and the reactivity of the substrates is controlled by the substitution of the double bond: while 2-cyclohexen-1-one shows a high reactivity, isophorone reacts very slowly. The solvent exhibits a strong influence since no reactivity was noticed in the oxidation of isophorone with TBHP on KF/alumina when using acetonitrile as solvent (5) whereas the reaction occurred with high yields in toluene (7). Isophorone is then both a possible industrial target in epoxidation of

activated olefins (8) and an interesting substrate for mechanistic considerations. The reaction with H$_2$O$_2$ can be extended to nonactivated olefins in the presence of benzonitriles (9) and it has been reported that the addition of a cationic surfactant such as *n*-dodecyltrimethylammonium bromide increased significantly the rate by improving the contact area between the organic and the aqueous phase (10). If the mechanism has been clarified, the choice of the solid and its activation can still be improved since previous authors used as catalyst the mixed oxide obtained by calcination of hydrotalcite, which is very active with hydrogen peroxide but was unable to activate TBHP (6). This work is devoted to the effect of the conditions of activation of hydrotalcite on its catalytic properties for the oxidation of 2-cyclohexen-1-one and isophorone with TBHP and H$_2$O$_2$, and to the comparison of hydrotalcites and different basic solids.

EXPERIMENTAL

Preparation of Materials

Hydrotalcites (HDTs) were prepared by coprecipitation at 338 K and pH 9 according to experimental procedures described in detail earlier (11). For the MgAl HDT, for instance, aqueous solutions containing (a) 0.75 mol/L of MgCl$_2$ · 6H$_2$O and 0.25 mol/L of AlCl$_3$ · 6H$_2$O (for a ratio Mg/Al = 3) and (b) 2 mol/L of NaOH and 0.5 mol/L of Na$_2$CO$_3$ were introduced by two electric pumps into a 4-L flask and mixed under vigorous stirring. The mixture was aged at 338 K for 18 h under stirring. The precipitate was washed several times until the solution was free of chloride ions (AgNO$_3$ test), then dried at 393 K. A series of MgAl HDTs referenced HT-*n* was prepared with different Al contents (Table 1).

The products of synthesis contain both Cl$^-$ (or NO$_3^-$) and CO$_3^{2-}$ as charge-compensating anions. They were exchanged by carbonates using a solution of Na$_2$CO$_3$: 2 g of HDT for 100 ml of a 0.2 M solution of Na$_2$CO$_3$ stirred at 343 K for 2 h.

KF1α was prepared with 1 mmol/g (3.7 wt% of KF) on an α-alumina (SPH 512 from Procatalyse) with a surface area of 10.5 m^2/g. After calcination at 723 K the surface area

TABLE 1

Ideal Formula, Surface Areas, and Amount of CO_2 Adsorbed on Hydrotalcites of Different Compositions

Sample	Formula	S_{BET} (m^2/g)	Pore size (nm)	CO_2 adsorbed (μmol/m^2)
MgCr	$Mg_{0.7}Cr_{0.3}(OH)_2(CO_3)_{0.17}$, 0.84 H_2O	216	2	0.95
MgFe	$Mg_{0.62}Fe_{0.38}(OH)_2(CO_3)_{0.16}$, 0.84 H_2O	159	2–13	0.8
CuAl	$Cu_{0.75}Al_{0.25}(OH)(CO_3)_{0.17}$, 1.2 H_2O	119	2–12	1.9
MgAl-3	$Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.13}$, 0.7 H_2O	234	12	1.8
HT-1A	$Mg_{0.716}Al_{0.284}(OH)_2(CO_3)_{0.164}Na_{0.0005}Cl_{0.0005}$, 0.458 H_2O	265	—	—
HT-1C	$Mg_{0.712}Al_{0.288}(OH)_2(CO_3)_{0.162}Na_{0.0003}Cl_{<0.0001}$, 0.500 H_2O	218	—	—
HT-2A	$Mg_{0.652}Al_{0.348}(OH)_2(CO_3)_{0.167}Na_{0.0005}Cl_{0.0002}$, 0.567 H_2O	254	—	—
HT-5	$Mg_{0.691}Al_{0.309}(OH)_2(CO_3)_{0.166}(NO_3)_{0.0003}K_{<0.0002}$, 0.569 H_2O	254	—	—
HT-13	$Mg_{0.745}Al_{0.255}(OH)_2(CO_3)_{0.153}(NO_3)_{0.0003}K_{0.0004}$, 0.469 H_2O	276	—	—
MgNiAl	$Mg_{0.17}Ni_{0.51}Al_{0.32}(OH)(CO_3)_{0.16}$	258	2	1.7
ZnAl	$Zn_{0.73}Al_{0.27}(OH)_2(CO_3)_{0.14}$	51	2–12	0.9
CoAl	$Co_{0.63}Al_{0.37}(OH)_2(CO_3)_{0.18}$	153	5–12	0.8
MgMnAl	$Mg_{0.65}Al_{0.23}(OH)_2(CO_3)_{0.15}$	200	2–12	—

of KF1α was 8.5 m^2/g. MgLa mixed oxides with different atomic ratios Mg/La $= 3$ was obtained by coprecipitation of Mg and La nitrates at a constant pH of 10. A F-exchanged hydrotalcite, described earlier (12), was used after calcination at 723 K.

Activation of the Catalysts

Catalysts (about 0.15 g of the as-made solid, reduced to about 0.1 g after activation) were first heated to 723 K in a flow of nitrogen (CuAl, CoAl, and ZnAl at 623 K), with a temperature program of 10 K/min, maintained for 8 h. In the experiments of rehydration the HDT was first decarbonated as usual, then cooled to room temperature and contacted with a flow of nitrogen saturated with the vapor pressure of water at this temperature for 1–48 h. Rehydration restores the HDT structure (except on MgCr samples) and also changes drastically the surface area and pore volume, as illustrated in Table 1 for MgAl HDT. Supported KF and MgLa mixed oxides were activated at 923 K and used without any rehydration.

Characterizations

X-ray powder diffraction patterns were recorded on a Phillips instrument using Cu$K\alpha$l radiation. The isotherm for N$_2$ adsorption at 77 K was determined on solids activated at 723 K in N$_2$ or air, then desorbed *in situ* at 473 K in a vacuum. Thermal analysis of the solids was performed on a TGDT A92 apparatus from SETARAM. The uptake of CO_2 was followed by volumetry, as reported earlier for the same series of samples (11). After activation in a flow reactor, the solid was transferred to the cell under argon using a glove bag, then outgassed at 673 K until a good vacuum (10^{-4} Pa) was reached. CO_2 was introduced in small increments at room temperature, and the isotherm of adsorption determined up to 133 Pa on a volumetric system equipped

with a Baratron capacitance manometer for precision measurements. CuAl and ZnAl samples, which decompose at lower temperatures, were treated at 623 K.

Catalytic Measurements

The epoxidations of 2-cyclohexen-1-one and of β-isophorone by diluted H_2O_2 (30%) and TBHP (5.5 M in decane) were studied in a batch reactor consisting of a three-necked 30-ml round-bottomed flask equipped with a condensor and maintained at room temperature in an oil bath. Cyclohexenone (Aldrich) or isophorone (Roche) (2 mmol) was introduced with 10 ml of solvent, with the required amount of oxidizing agent, for instance 4 mmol of TBHP. The reactor was swept with a small flow of nitrogen to remove CO_2 from the atmosphere and stirred at 450 rpm. The catalyst (typically 0.15 g of the as-made sample, reduced to 0.1 g after calcination), freshly activated at 723 K (or 623 K for CuAl and ZnAl), was introduced and the progress of the reaction followed by gas chromatography using a DB5 column. The amount of oxygen evolved by the reaction medium was measured by volumetry in order to check the balance of oxygen in the reaction.

RESULTS

Characterization of the Catalysts

The characterization of hydrotalcites was reported earlier (11). From XRD patterns, all hydrotalcites samples are pure hydrotalcites of good crystallinity. The chemical compositions of the different solids are reported in Table 2. The calcination of hydrotalcites results in mesoporous mixed oxides of high surface area. In all cases the XRD pattern is then that of the divalent oxide amorphous matrix. We report in Fig. 1 the isotherms of CO_2 adsorption determined on HDT samples decarbonated at 723 K.

TABLE 2

Surface Areas and Porosities of a MgAl-3 Hydrotalcite after Calcination at 723 K and Further Rehydration at Room Temperature for Different Periods of Time

	As made	Treated at 723 K	Rehydration		
			5 h	15 h	48 h
S_{BET} (m^2/g)	95	265	50	19	12
Pore volume (ml/g)	0.4	0.86	0.26	0.1	0.06

The MgLa mixed oxide appears from XRD patterns as a biphasic system containing both brucite and La carbonate (Fig. 2). The surface area of this mixed oxide reaches 45 m^2/g after calcination at 923 K. The solid most probably consists of a layer of La oxide deposited on magnesia. DTA analysis shows that the solid is decarbonated only above 980 K (Fig. 3).

The XRD spectrum of KF1α contains the diffraction lines of the alumina support, with weak lines due to K$_3$AlF$_6$, which shows the low reactivity of α-alumina toward KF. The solid can then be described as a well-dispersed fluoride at the surface of the support. The small change of surface area is also indicative of the marginal modification of the support. The decarbonation temperature in DTG was about 773 K. Therefore this thermal analysis suggests that the most basic solid is the MgLa mixed oxide and that HT-13 contains the highest number of basic sites.

Epoxidation of Cyclohexenone with H$_2$O$_2$

Catalytic properties of calcined hydrotalcites. The epoxidation of 2-cyclohexen-1-one by hydrogen peroxide
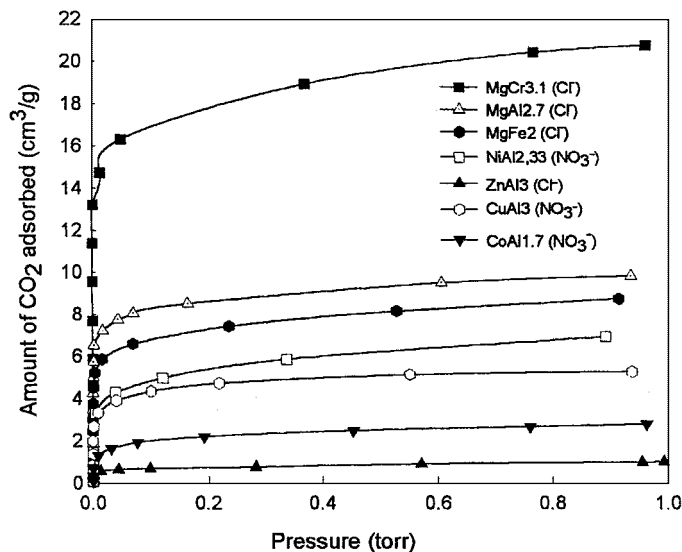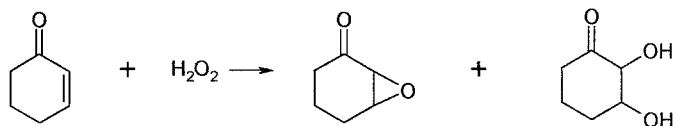
SCHEME 1. Epoxidation of 2-cyclohexen-1-one by hydrogen peroxide.

(Scheme 1) follows a first order relative to the olefin, as illustrated in Fig. 4. A very important parameter of activity appeared to be the composition. The comparison of HDTs of different compositions calcined at 723 K is reported in Fig. 5. The H$_2$O$_2$ selectivities are reported in Table 3. It appears that HDTs containing transition metals lead to a high selectivity to oxygen and correspondingly to a low reactivity for epoxidation, except for CuAl HDT, which shows the highest rate in spite of a high rate of H$_2$O$_2$ decomposition. The Fenton reaction can lead to the decomposition of H$_2$O$_2$ and is the main process here except in the case of MgAl and ZnAl, which are hardly reducible. It has to be mentioned that when epoxidation occurs, the selectivity for the epoxide remains very high.

The second step was to check whether the catalyst weight could have any influence on the results. Table 4 illustrates the fact that decreasing the amount of catalyst by a factor of 3 does not affect the final conversion after 6 h but controls the initial rate, as expected. The selectivity to oxygen of MgFe catalysts is unaffected by a lower mass of sample and decomposition of H$_2$O$_2$ remains predominant. With the exception of this MgFe, the initial rate of epoxidation on these solids is roughly related to the number of basic sites evaluated by the rate of isophorone isomerization, as reported in Table 4.

Comparison of H$_2$O$_2$ and TBHP. The comparison was performed with MgAl HDT calcined at 723 K, using toluene as solvent of TBHP (ratio oxidizing agent/substrate $= 4$). The results are reported in Fig. 6 and show that if high

FIG. 1. Isotherms of CO$_2$ adsorption on hydrotalcites of different compositions decarbonated at 723 K.
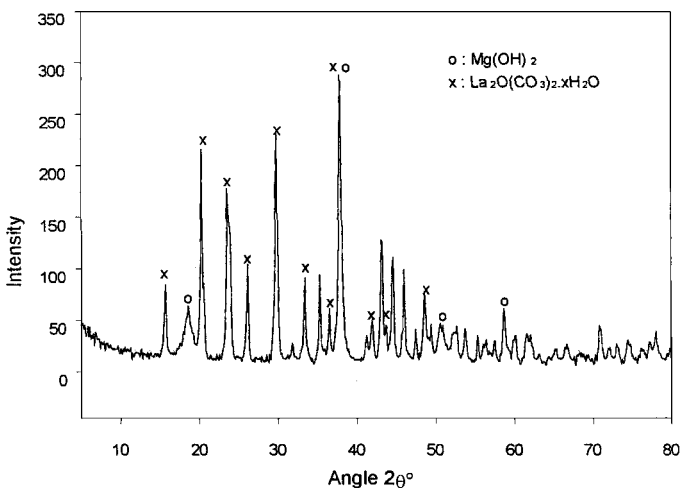
FIG. 2. Powder XRD pattern of MgLa mixed oxide.

TABLE 3

Comparison of Different Hydrotalcites for the Oxidation of 2-Cyclohexen-1-one by Hydrogen Peroxide at 298 K, and Isomerization of Isophorone at 308 K

| | Epoxidation of cyclohexenone | | | |
Sample	Final yield after 6 h (%)	$-r_{Ao} \times 10^3$ (mol L^{-1} min^{-1})	Selectivity O$_2$ after 6 h (%)	Rate of isophorone isomerization $\times 10^5$ (mol s^{-1} g^{-1})
MgAl	94	3.01	0	5.3
CuAl	93	3.52	51	3.3
MgMnAl	46	0.27	99.6	—
MgCr	38	0.51	70.5	0.3
MgNiAl	19	0.41	81.4	1.9
ZnAl	13	0.74	0	2.1
CoAl	9	0.30	87	1.4
MgFe	5	0.00	67	6.6

TABLE 4

Effect of the Catalyst Mass on the Rate of Oxidation of 2-Cyclohexen-1-one by Hydrogen Peroxide

Sample	Cat/subst. (mg/mmol)	Final yield (%)	O$_2$ selectivity (%)	$-r_{Ao} \times 10^3$ (mol L^{-1} min^{-1})
MgAl	150	94	0	3.01
MgAl	49	91	0	1.1
MgAl	31	92	0	1.26
MgFe	150	5	67	0.00
MgFe	72	10	65	0.00
MgFe	49	0	64	0.00

Note. Reaction time: 6 h.
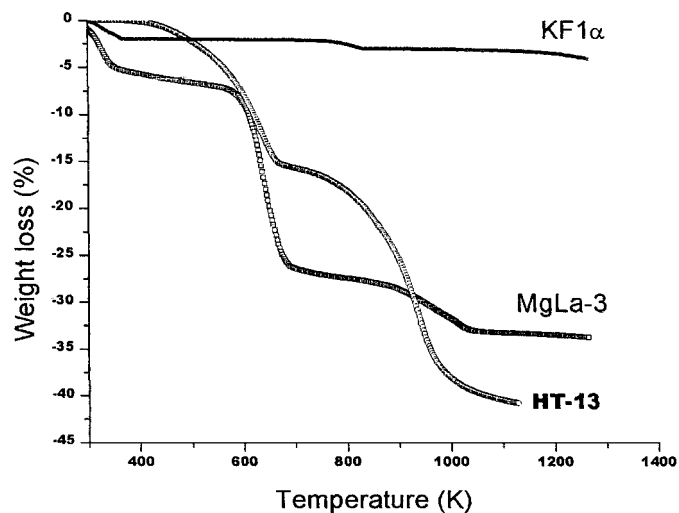
FIG. 3. Differential gravimetric analysis of MgLa, KF1α, and HT-13.

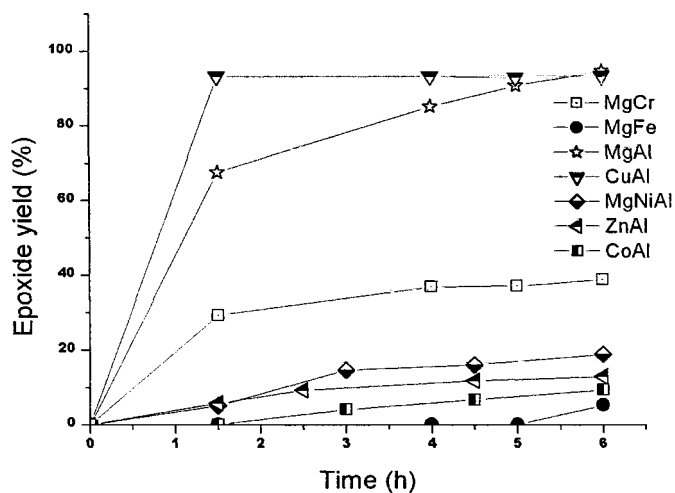**FIG. 5.** Activities of calcined hydrotalcites for the epoxidation of 2-cyclohexen-1-one by hydrogen peroxide at room temperature.

FIG. 4. Illustration of the first-order kinetics on 2-cyclohexen-1-one epoxidation on hydrotalcites: (a) MgAl, (b) CoAl, and (c) MgNiAl.
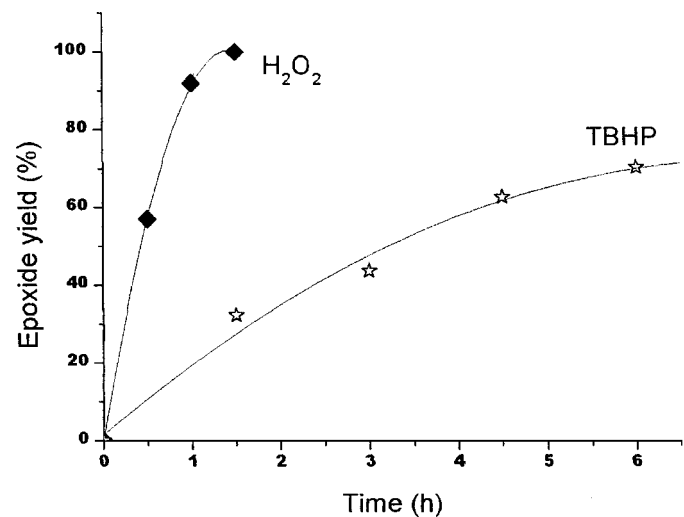

FIG. 6. Comparison of hydrogen peroxide and TBHP as reactants for 2-cyclohexen-1-one oxidation at room temperature on MgAl-3.

TABLE 5

Effect of Solvent Polarity in the Oxidation of Cyclohexene by TBHP on Calcined HT-13

Solvent	Final yield (%)	Initial rate $-r_{Ao} \times 10^3$ (mol L^{-1} min^{-1})	Polarity μ (10^{-30} C m)
Water	100	3.20	5.9
n-Heptane	74.2	0.80	0.0
Toluene	70.4	0.75	1.0
1,2-Dimethoxyethane	9.5	—	5.7
Acetone	7	—	9.0
1,2-Dichloroethane	5.3	—	6.1
2-Propanol	5	—	5.5
Acetic acid	0.00	0.00	5.6

Note. Reaction time: 6 h.

conversions are reached with both oxidants, the rate is significantly lower in the case of TBHP/toluene. This low rate may be due to the choice of solvent and its effect was therefore checked. The results of Table 5 report the effect of the solvent on the reaction of cyclohexenone and TBHP and show that the choice of the solvent is important, as expected for an ionic mechanism. The best solvent is water, but heptane and toluene are also acceptable.

Rehydration of the mixed oxides and influence of basicity. The relation of catalytic activity with basicity suggested rehydration of the mixed oxide to meixneiritelike materials. It was demonstrated earlier that the layered structure can be restored by treatment with water vapor, giving a solid base with a high density of sites. The results are reported in Table 6: the activity for the epoxidation of 2-cyclohexen-

TABLE 6

Effect of Rehydration of the Mixed Oxide on the Rate of 2-Cyclohexen-1-one Oxidation by TBHP after 6 h of Reaction Time in Methanol as Solvent

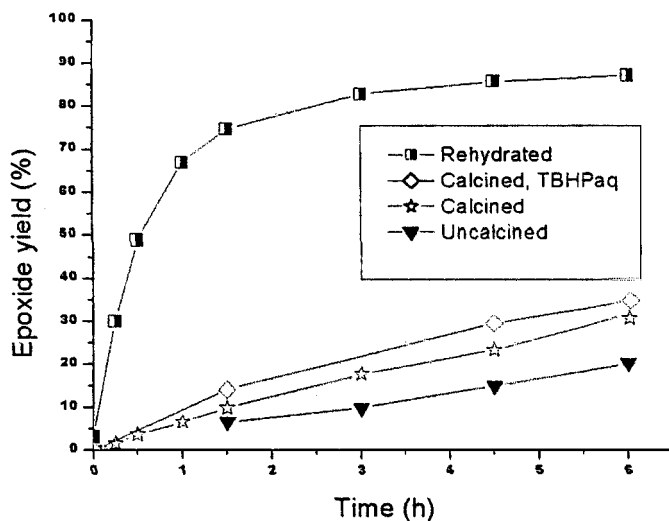| Catalyst	% Final yield	$-r_o \times 10^3$ (mol L^{-1} min^{-1})
MgAl-3	31.6	0.31
MgAl-3[a]	33.5	0.44
MgAl-3 rh(6)	87	3.57
HT-5	27	0.14
HT-5 rh(1)	37	0.44
HT-5 rh(3)	83	1.78
HT-5 rh(5)	72	0.76
HT-5 rh(7)	55	0.29
HT-13 rh(3)	81.5	1.03
HT-13 rh(6)	80	1.27
HT-1A	26	0.24
HT-1C	29	0.19
HT-1A rh(3)	48	0.38
HT-2A rh(3)	27	0.21

[a] TBHP, 70% aqueous solution.

FIG. 7. Effect of the activation conditions on the catalytic properties of MgAl-3 hydrotalcite for the oxidation of 2-cyclohexen-1-one by TBHP at 298 K using methanol as solvent.

1-one by TBHP increases significantly after rehydration, as expected for a reaction catalyzed by OH. The rehydration is slow: HT-3 used after calcination with TBHP in decane or with aqueous TBHP exhibits the same 33% epoxide yield, which is increased to 87% after rehydration. The initial rate goes through a maximum after about 3 h of rehydration time. The effect is general and observed on several samples, such as HT-3, HT-5, and HT-13; it is illustrated in Fig. 7 for HT-3. It can be noticed that the epoxidation of 2-cyclohexen-1-one by TBHP on rehydrated hydrotalcite shows a low sensitivity to water added to the reaction medium via the oxidant. Therefore the maximum of activity as a function of the time of rehydration has to be related not to a kinetic effect of water but to the decrease of surface area (Table 1) induced by the restoration of the layered structure.

The Al content of HDT has also a clear influence on activities measured both without or after rehydration, as reported in Table 7. The higher activity is observed at a

TABLE 7

Influence of the Al Content of MgAl Hydrotalcite on the Catalytic Properties of Hydrotalcites for the Epoxidation of 2-Cyclohexen-1-one by TBHP

Catalyst	Mg/Al	pH	Preparation		Epoxide yield (%)	
			Base	Salt	Calcined	Rehydrated
HT-13	2,9	10	K_2CO_3	Nitrates	33	87
HT-5	2,2	9	K_2CO_3	Nitrates	27	83
HT-1A	2,5	9	Na_2CO_3	Chlorides	26	48
HT-2A	1,9	9	Na_2CO_3	Chlorides	17	27

Note. Reaction time: 6 h.

TABLE 8

**Comparison of Different Solid Bases as Catalysts for
2-Cyclohexen-1-one Epoxidation Using TBHP as Oxidizing Agent**

Catalyst	Rate of isophorone isomerization $\times 10^4$ (mol g^{-1} min^{-1})	Epoxide yield (%)
KF/αAl$_2$O$_3$	0.7	82.4
MgLa	4	82.1
HT-13 rh(6)	29.3	87

Note. Reaction time: 6 h.

Mg/Al ratio of 3, regardless of which alkaline cation is used in the synthesis. A maximum of activity at Mg/Al $=3$ has been reported for many base-catalyzed reactions, including Knoevenagel condensation (13), aldolization (14), and dibenzothiophene oxidation to sulfone (15), and is therefore attributed to a higher basicity of the solid.

Some other solid bases are compared in this process in order to check the influence of basicity in the reaction (Table 8). Yadav and Kapoor (5) first reported KF/Al$_2$O$_3$ as a good catalyst, and it is observed here that comparable yields can be reached using TBHP and rehydrated MgAl HDT or MgLa mixed oxides, which are strong solid bases. This behavior is consistent with a base-catalyzed mechanism. The present series of solid bases permit taking into account both the basic strength and the number of active sites. We report in Table 8 the number of basic sites estimated by the rate of the zero-order isomerization of isophorone compared to the yield in cyclohexenone epoxidation. No direct relationship could be observed between the number of basic sites and the yield. KF1α, with a small number of basic sites, is as active as MgLa. The high activity of HT-13 comparable to that of MgLa can be attributed to a compensation effect of the lower strength by a large number of sites.
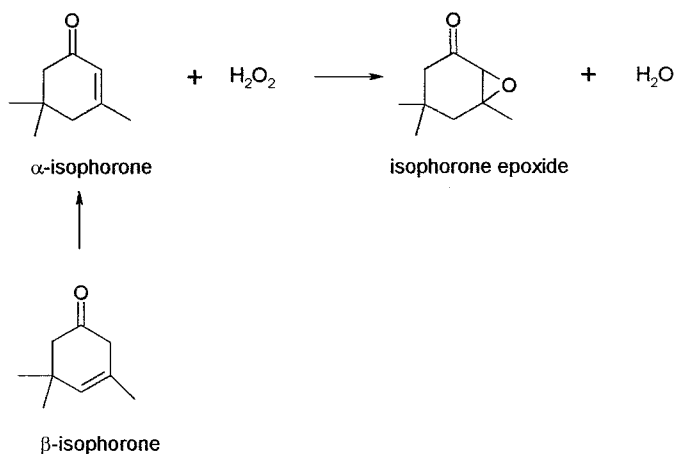
Oxidation of β-isophorone with hydrogen peroxide. β-Isophorone is not an activated olefin and cannot be epoxidized by a basic mechanism. The epoxidation of α-

TABLE 9

Yield in Epoxide after 24 h in the Oxidation of β-Isophorone by H$_2$O$_2$ on MgAl Hydrotaclcite and MgLa Mixed Oxide

Catalyst	Rehydration time (h)	Reaction temp (K)	Reactants (mmol)		Epoxide yield (%)
			H$_2$O$_2$	Isophorone	
HT-5	3	293	2,7	2,7	N.R.
HT-5	3	333	2,7	2,7	N.R.
HT-5	5	293	2,7	2,7	N.R.
HT-F	0	293	9,5	2,7	8,9
MgLa-3	0	293	9,5	2,7	68

Note. Solvent: methanol (10 ml).

SCHEME 2. Reactions of α- and β-isophorone with hydrogen peroxide.

isophorone is in principle possible, with a low reactivity compared to cyclohexenone. No reaction was however observed using TBHP on HDT regardless of the procedure of activation. The oxidation with H$_2$O$_2$ was studied using rehydrated MgAl HDT: the isomerization of β-isophorone to α-isophorone is complete in a few minutes, so the products are those of the oxidation of α-isophorone (Scheme 2). When water was used as solvent a biphasic system was obtained and the analysis of the reaction medium became difficult, so toluene and methanol were preferred as solvents since they gave monophasic solutions.

The results obtained in different conditions are reported in Table 9. With a H$_2$O$_2$/isophorone ratio of 1, HDT gave poor results regardless of the conditions of activation. Earlier work (16) reported better results in an excess of oxidant and long reaction times, so the low rate at this ratio is attributed to a kinetic law involving competitive adsorption of the reactants. The more basic MgLa mixed oxide was able to convert isophorone to its epoxide with a yield of 68% after 24 h at room temperature using methanol as solvent and an excess of H$_2$O$_2$. The selectivity to the epoxide was high and the 24% remaining was unreacted α-isophorone. F-exchanged hydrotalcite exhibited a low activity. This pattern is representative of a reactivity dominated by the basic strength of the catalyst: with isophorone of low reactivity a relatively strong base such as MgLa mixed oxide is required.

DISCUSSION

The results reported here include the low activity of raw hydrotalcite or of the mixed oxide, and its promotion upon rehydration are in line with a mechanism catalyzed by basic hydroxyls. With a substrate of high reactivity, such as cyclohexenone, the effect of basic strength is small and mild bases appear to be active. This explains why the protocol of activation is not critical in that case and why oven dried HDT can be active, as reported by Yamaguchi *et al.* (10). With

substrates of low reactivity, stronger bases are required. Let us recall here that in earlier work on the epoxidation of α-isophorone on solid bases (calcined HDT and KF/γ Al$_2$O$_3$) the best yield in epoxide was reported to be 66% after 72 h, with a oxygen selectivity limited to 41%. The work of Hutter *et al.* (17, 18) and Beck *et al.* (4) has been relative to the use of TBHP, so the epoxidation by H$_2$O$_2$ was far less documented. The MgLa catalyst works approximately in the same conditions as HDT but gives a significantly higher activity, since the same yield is reached in 24 instead of 72 h, with a high selectivity to H$_2$O$_2$, thus illustrating the importance of basic strength in this reaction.

Our results can be compared with those on titania–silica aerogels reported by Hutter *et al.* (17) for the oxidation by TBHP: in both cases a good selectivity to the epoxide was noticed (>98%) in spite of the different solvents— ethylbenzene for Ti catalysts and methanol for MgLa oxides. The yield reported on Ti catalyst was about 70% after 16 h at 323 K compared with the 47% after 9 h and 67% after 24 h at room temperature observed here. It was reported earlier (16) that a faster rate could be obtained at 333 K with no loss of TBHP selectivity. It can therefore be supposed that the result of basic catalysis can be improved.

In conclusion, TBHP can indeed be activated by hydrotalcites provided they are decarbonated, then rehydrated. The main difference between basic catalysts and titanosilicates is that the former work better in an excess of H$_2$O$_2$, while the Ti catalyst works well in an excess of isophorone. This may have practical implications for the separation of the products. The MgLa mixed oxide is mainly interesting for substrates of low reactivity, such as α-isophorone. This catalyst is not as active as Mg–Al–O–*t*–Bu hydrotalcite, reported by Choudary *et al.* (19), which reaches a yield of 90% in 5 min with 2-cyclohexen-1-one; however it shows an interesting possibility of recycling after being obtained from activation at 923 K—the solid is thermally stable and can therefore be regenerated by calcination.

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