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# Isophorone Isomerization as Model Reaction for the Characterization of Solid Bases: Application to the Determination of the Number of Sites

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**The isomerization of $\beta$-isophorone to $\alpha$-isophorone has been investigated as a model reaction characteristic of basic sites. A zero order is observed at 308 K on many solid bases, thus allowing a measure of the total number of active sites. On MgAl mixed oxides obtained by decarbonation of hydrotalcites, this number corresponds to the number of sites adsorbing $CO_2$, and a linear correlation is observed between the initial rates of isomerization of isophorone and those of Claisen–Schmidt aldolic condensation, thus showing that both reactions are catalyzed by basic sites. By rehydration the mixed oxides are converted to meixneritelike materials, with an increase of activity for isomerization, as for aldolization. The rate of isomerization has been used to measure the number of sites on a series of solid bases, the basic strength of which was estimated by the temperature of decarbonation. With this criterion, Ba hexa-aluminate decarbonated below 550 K appears to be a weaker base than hydrotalcite and $La_2O_3$/MgO decarbonated above 650 K and KF/$\alpha Al_2O_3$ decarbonated above 850 K. The activities of these solids for isophorone isomerization are, however, proportional to the number of sites determined by desorption of $CO_2$.**

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

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## INTRODUCTION

While a large number of solids and experimental methods have been proposed to characterize acid catalysts such as zeolites, clays, mixed oxides, and sulfates, the situation is quite different in the field of solid bases. Indeed the experimental methods of characterization of basicity are to still to be established, and a simple tool allowing measurement of the number of sites in the conditions of reaction would be useful. A model solid base such as hydrotalcitelike materials (HDT) can help in this purpose. The mixed oxides obtained by decarbonation are mesoporous and basic and their properties can be tailored by the nature of the cations, the compensating anions, and calcination temperature (1–3). The synthesis of these HDTs is well documented (4–6). The decarbonated materials obtained by appropriate activation catalyze a variety of organic transformations, such as aldol condensations (7–9), epoxidation of activated olefins with hydrogen peroxide (10), Claisen–Schmidt condensation (11), selective reduction of aldehydes and ketones by hydrogen transfer from alcohols (12), glycerolysis of fats to monoglycerides (13), and alkylation of phenols by alcohols (14).

Most of these reactions are bimolecular, and often they obey competitive mechanisms in which the rate goes through a maximum for a certain ratio of the reactants (15, 16). Therefore the choice of the initial concentration of reactants is critical since the optimum conditions are likely to be different for each sample. A comparison of catalysts requires, thus, a complex kinetic study to separate the respective effects of adsorption and rate constants. By contrast, monomolecular reactions involving a single adsorbed species are much simpler to analyze. The gas-phase conversion of isopropanol (17–19) and of 2-methyl-3-butyn-2-ol (20, 21) has been proposed for this purpose. Both reactions suffer a strong deactivation due to formation of heavy products, by aldolization of acetone in one case (21) and polymerization of acetylene in the other (22). Therefore they have been described as simple diagnostic tools which can show the acid/base reactivity of a solid (21) but cannot be used to measure the number of active sites. The conversion of acetonylacetone has also been proposed (23) but appears to be a first-order reaction and therefore is less suitable for the determination of the number of active sites (16).

The isomerization of $\beta$-isophorone to $\alpha$-isophorone (Scheme 1) is a simple monomolecular reaction catalyzed by hydrotalcites, with a thermodynamic equilibrium displaced toward $\alpha$-isophorone at low temperature (24). The acid-catalyzed reaction occurs as a parallel reaction of the epoxidation by *tert*-butylhydroperoxide on titania–silica gels at 353 K (25): the conversion of $\beta$-isophorone of about 7% on pure Ti–$SiO_2$ falls to zero on addition of small amounts of $NaHCO_3$ but increases to 95% on addition

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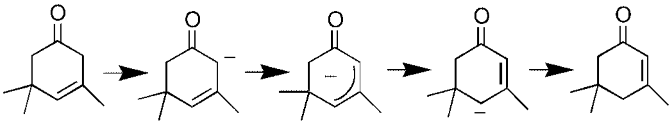

**SCHEME 1.** Basic mechanism for the isomerization of isophorone.

of $BaCO_3$ and NaOH and to 60% on addition of MgO. Acid catalysis is then slower than basic catalysis in this case and cannot perturb the experiments. Therefore this simple model reaction has been studied as a tool for the characterization of basic solids.

## EXPERIMENTAL

### *Preparation of Hydrotalcite Precursors*

HDTs were prepared by coprecipitation at 338 K and pH 9 according to experimental procedures described in detail earlier (4–6, 26). The chemicals used were Mg and Al nitrates and K hydroxide and carbonates, except for HT-3, which was prepared from Na bases. For the MgAl HDT, for instance, aqueous solutions, the first containing 0.75 mol/L of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.25 mol/L of $Al(NO_3)_3 \cdot 9H_2O$ (for a Mg/Al ratio of 3), the second containing 2 mol/L of KOH and 0.5 mol/L of $K_2CO_3$, 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. They were exchanged by carbonates using a solution of $Na_2CO_3$ : 2 g of HDT for 100 ml of a 0.2 M solution of $Na_2CO_3$ stirred at 343 K for 2 h. The chemical compositions of the final solids are reported in Table 1.

### *Synthesis of Other Solid Bases*

KF/alumina (KFA) was purchased from Aldrich and a sample of KF on $\alpha$-alumina, refered to as KF1$\alpha$, was prepared with a content of 1 mmol/g (3.7 wt% KF) on $\alpha$-alumina (SPH 512 from Procatalyse) with a surface area of 10.5 $m^2/g$. After calcination at 823 K the Aldrich sample of KF/alumina shows a surface area of 14.9 $m^2/g$ and KF1$\alpha$ a surface area of 8.5 $m^2/g$. MgLa mixed oxides with different Mg/La atomic ratios (2, 3, and 20) were obtained by coprecipitation of Mg and La nitrates at a constant pH of 10. A sample of Ba hexa-aluminate was prepared by sol–gel following the procedure reported by Artizzu-Duart *et al.* (27).

**TABLE 1**

**Ideal Chemical Formula of the Hydrotalcites Converted to the Carbonate Form, and Surface Areas after Decarbonation at 723 K**

| Catalyst | Surface area ($m^2/g$) | Cell composition |
|---|---|---|
| HT-6 | 261 | $Mg_{0.64}Al_{0.36}(OH)_2(CO_3)_{0.17}$ 1.2$H_2O$ |
| HT-21 | 197 | $Mg_{0.66}Al_{0.27}(OH)_2(CO_3)_{0.15}$ 0.6$H_2O$ |
| HT-3 | 230 | $Mg_{0.66}Al_{0.33}(OH)_2(CO_3)_{0.17}$ 0.6$H_2O$ |
| HT-13 | 276 | $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.15}$ 0.47$H_2O$ |
| HT-14 | 280 | $Mg_{0.8}Al_{0.2}(OH)_2(CO_3)_{0.18}$ 0.52$H_2O$ |
| HT-15 | 310 | $Mg_{0.83}Al_{0.17}(OH)_2(CO_3)_{0.19}$ 0.24$H_2O$ |
| HT-16 | 263 | $Mg_{0.85}Al_{0.15}(OH)_2(CO_3)_{0.24}$ 0.5$H_2O$ |

**TABLE 2**

**Surface Areas and Porosities of a MgAl 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 |
| $S_{BET}$ ($m^2/g$) | 95.3 | 265.2 | 50.2 | 19.1 | 11.7 |
| Pore volume (ml/g) | 0.41 | 0.85 | 0.26 | 0.099 | 0.06 |

### *Activation of the Catalysts*

Catalysts were first heated in a flow of nitrogen to 723 K, maintained for 8 h and reached with a temperature program of 10 K/min. In the experiments of rehydration the HDT was first decarbonated, then cooled to room temperature and contacted with a flow of nitrogen saturated with the vapor pressure of water at this temperature for 12 h. The excess water was removed by treatment under dry $N_2$ at 353 K. Rehydration restores the HDT structure and also changes drastically the surface area and pore volume, as illustrated in Table 2 for MgAl HDT. The rehydrated samples are denominated HDTR.

MgLa mixed oxides were activated 923 K and supported KF and Ba hexaaluminate at 723 and 923 K. All were used without any rehydration.

### *Characterizations*

Chemical compositions were determined by ICP analysis of the solutions obtained by acid attack of the solids. X-ray powder diffraction patterns were recorded on a Siemens D500 instrument using Cu$K\alpha$1 radiation. The BET surface areas and BJH pore size distributions were determined from adsorption–desorption isotherms of $N_2$ at 77 K. This isotherm was determined on solids activated at 723 K in $N_2$ or air, then desorbed *in situ* at 473 K in a vacuum. In order to prevent dehydration, the rehydrated samples were evacuated at room temperature until a residual pressure of 5 mPa was reached. The basic properties were estimated by analyzing the amount of $CO_2$ contained in the effluents during the thermal analysis of a solid, using a TGDT A92 from SETARAM coupled with a mass spectrometer.

### *Catalytic Measurements*

The isomerization of $\beta$-isophorone and Claisen–Schmidt condensation were studied in a batch reactor composed of a three-necked 50-ml round bottomed flask, heated at 308 K in an oil bath. Ten milliliters of isophorone (66 mmol, Roche) was introduced with 40 ml of heptane as solvent, forming a 1.3 M solution. The reactor was swept with a small flow of nitrogen to remove $CO_2$ from the atmosphere and stirred at 1000 rpm. When the thermal equilibrium was reached, the catalyst (0.15 g of the as-made sample, reduced to about 0.1 g after pretreatment), freshly activated at 723 K, was introduced and the progress of the reaction followed by gas chromatography using a DB5 column.

For the aldol condensation of acetone with benzaldehyde, 0.51 ml (5.02 mmol) of aldehyde was used with 11.85 ml (0.161 mol) of acetone and the reaction was performed at 273 K in an ice bath.

## RESULTS AND DISCUSSION

### *Characterization of the Original Catalyst Samples*

The characterization of hydrotalcites was reported earlier (28). From XRD patterns all hydrotalcites samples are pure hydrotalcites of good crystallinity. The calcination of hydrotalcites results in mesoporous mixed oxides of high surface area. In all cases the XRD pattern is that of the divalent oxide amorphous matrix.

Upon rehydration, the well-known phenomenon of restoration of the layered structure occurs (15, 29), with a parallel loss of surface area, as illustrated in Table 2. After about 18 h the original XRD is obtained with high crystallinity and therefore a comparable crystal size. The rehydrated solid shows no porosity and a surface corresponding to the external area of the crystals (Table 2).

The MgLa mixed oxides appear from XRD patterns as biphasic systems containing both Mg hydroxide and La carbonate (Fig. 1). The surface area of this mixed oxide reaches 54.8 m$^2$/g after calcination at 923 K (Table 3). After calcination the solid most probably consists of a layer of La oxide deposited on magnesia. The DTA trace contains three weight losses and suggests that the solid is completely decarbonated and dehydroxylated at about 1000 K (Fig. 2).

**TABLE 3**

**Composition of MgLa Mixed Oxides after Calcination at 923 K**

| Catalyst | Mg (wt%) | La (wt%) | C (wt%) | Surface area (m$^2$/g) |
|---|---|---|---|---|
| MgLa-2 | 12.8 | 39.4 | 4.5 | 28 |
| MgLa-3 | 6.4 | 52.6 | 3.9 | 37 |
| MgLa-20 | 9.9 | 45.2 | 4.4 | 54.8 |

The XRD spectrum of KF1$\alpha$ (Fig. 3) contains the diffraction lines of the $\alpha$-alumina used as support, with very weak lines due to $K_3AlF_6$. The absence of this solid phase evidences the low reactivity of $\alpha$-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 DTA was well below 500 K for KFA (not shown) but reached 800 K on KF1$\alpha$ (Fig. 4).

Barium hexa-aluminate was amorphous after activation. The thermal analysis shows an intense peak of $CO_2$ at 523 K (Fig. 4). The comparison shows that $CO_2$ was lost at quite different temperatures for these solids, which permits a scale of basic strength to be obtained in which Ba aluminate is a mild base, significantly lower than that of HDT, supported La oxide, or supported KF. It was reported before that HDTs of different Mg/Al ratios show differences in the number of sites but comparable strengths (28).

### *Kinetics of Isophorone Isomerization on Rehydrated Hydrotalcites*

The kinetics of the isomerization of $\beta$-isophorone to $\alpha$-isophorone have been determined on HT-21 (Mg/Al = 2.4)

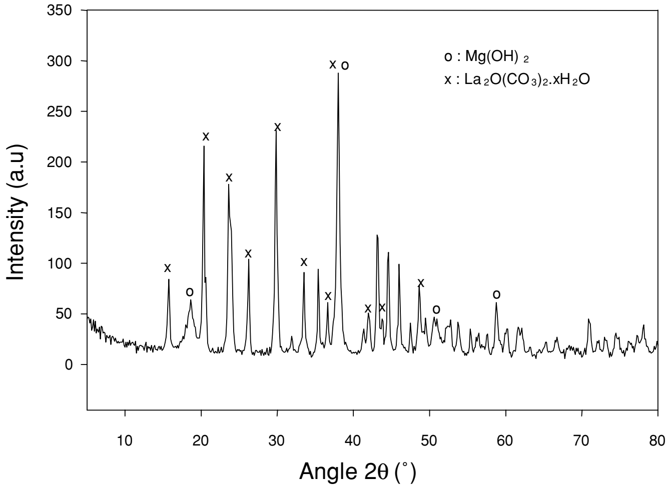

**FIG. 1.** XRD pattern of MgLa-3 mixed oxide.

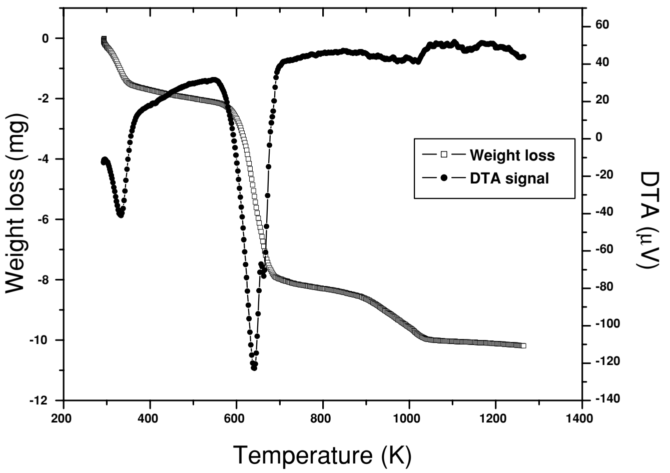

**FIG. 2.** Thermal analysis of MgLa-3 mixed oxide.

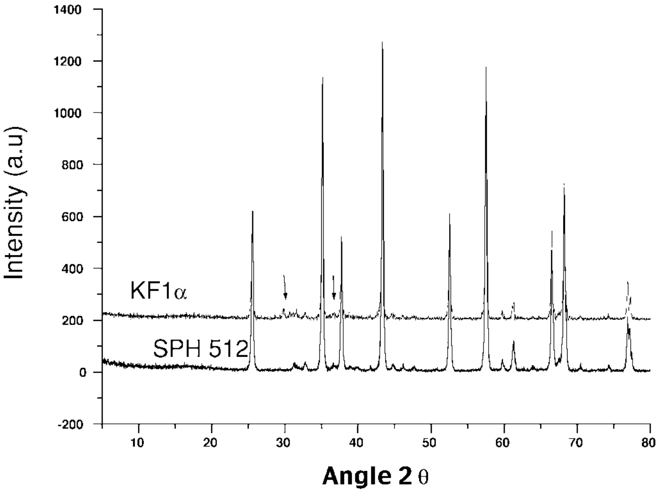

**FIG. 3.** XRD pattern of KF1$\alpha$ calcined at 723 K. The arrows indicate the diffractions due to $K_3AlF_6$.

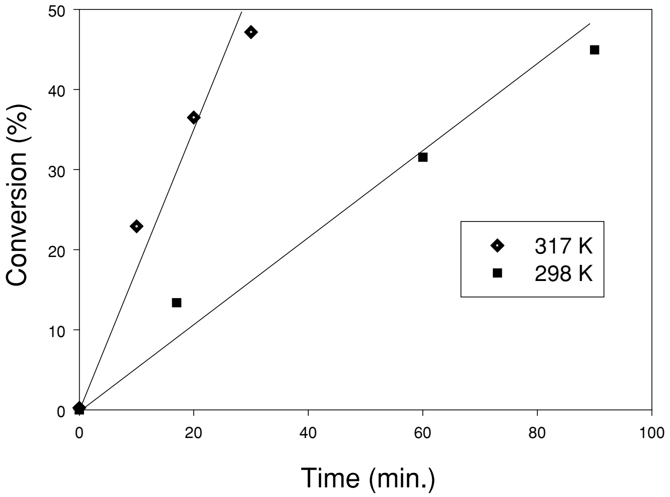

**FIG. 5.** Kinetics of isophorone isomerization on HT-21 at 298 and 317 K.

first calcined then rehydrated in $N_2$ saturated with water. The only product of the reaction is $\alpha$-isophorone and the reaction is zero order relative to the substrate at different temperatures (Fig. 5). In that case the rate equation is reduced to $r = k$, and the initial rate is equal to the rate constant. The determination of the kinetic rate constant at different temperatures allows calculation of the true activation energy of the surface reaction (Fig. 6), which is found equal to 78 kJ/mol$^{-1}$. This value in turn permits calculation of the number of sites from the theory of Eyring, assuming that the activation entropy is negligible. This entropy represents the difference in entropy between the adsorbed state and the activated complex, and since the largest term in entropy is due to translation, the assumption that the activation entropy is negligible is quite acceptable, in particular for zero-order kinetics, i.e., a strong adsorption.

According to the theory of absolute rate, the rate constant can be written

$$k_r = kT/hB_0 \exp(-E/\mathrm{RT}) \exp(\Delta S/R),$$

in which $k$ and $h$ are the Boltzmann and Planck constants, $E$ and $\Delta S$ the enthalpy and entropy of activation, and $B_0$ the number of sites. From this formula $B_0$, the number of sites active for the reaction, is found to equal 0.4 mmol/g, corresponding to 1/10 of the total Al atoms in the sample. The value determined directly by $CO_2$ adsorption on a rehydrated sample of close composition (Mg/Al = 2.7) was 0.35 meq/g, in good agreement with the present result.

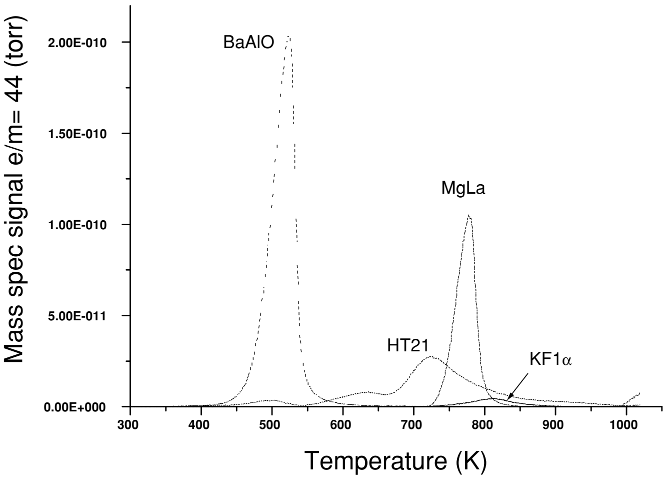

**FIG. 4.** Desorption of $CO_2$ followed by mass spectrometry during the thermal analysis of hydrotalcite HT-21, KF1$\alpha$, LaMg mixed oxide, and barium hexa-aluminate.

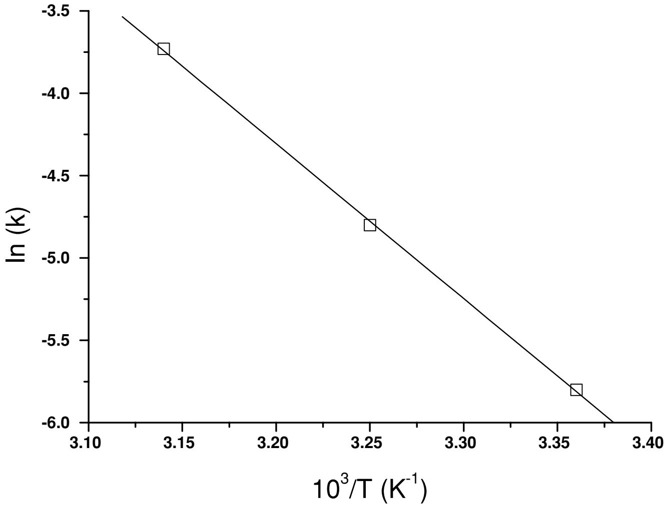

**FIG. 6.** Arrhenius plot of the rate constants for isophorone isomerization on rehydrated HT-21.

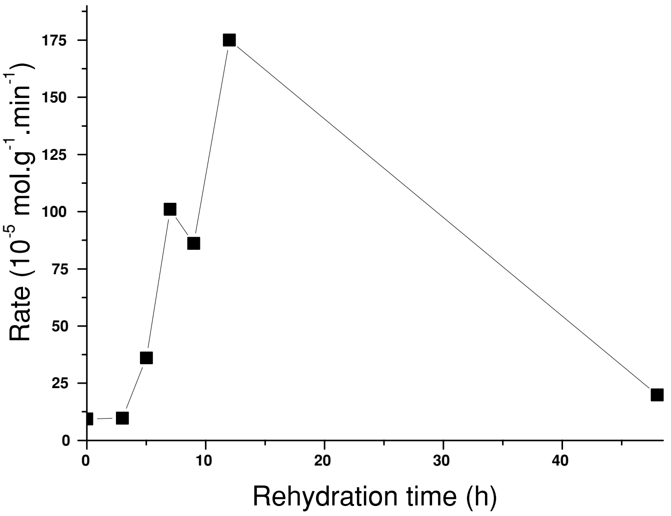

**FIG. 7.** Effect of rehydration of HT-3 on the activity for isophorone isomerization at 308 K.

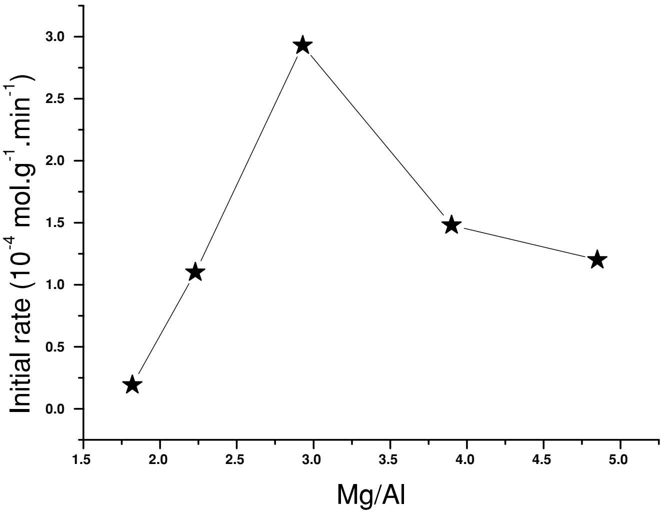

**FIG. 8.** Effect of Mg/Al ratio on the rate of isophorone isomerization at 308 K on samples rehydrated for 12 h.

## *Effect of Rehydration of the Sample*

Figure 7 reports the effect of rehydration of the mixed oxide obtained by calcination of HT-3: as for aldol condensations (7–9), the rate increases when the solid is rehydrated and then decreases after prolonged contact with water. Rehydration is slow and probably limited by the diffusion of water within the crystals. The rehydration of the surface is faster than that of the bulk, since it takes only 12 h to reach the maximum activity but 2 days to recover the original crystallinity. At that time the XRD pattern shows the formation of a layered meixnerite structure and a sharp decrease in surface area, from 265 $m^2$/g after decarbonation to 12 $m^2$/g after 48 h of rehydration (Table 2). The decrease of activity for isophorone after 12 h can then reflect the lower accessibility at the basic sites of meixnerite, as proposed by Roelofs *et al.* (29).

Isophorone isomerization was used to investigate the catalytic properties of a series of HDTRs obtained with Mg/Al ratios in the range 1.77–5.66. Activity goes through a maximum for a ratio of 3 (Fig. 8), as for Knoevenagel condensation of benzylacetone and ethyl cyanoacetate (13). On this series of samples of HDTR a good correlation exists between the rates of isophorone isomerization and Claisen–Schmidt condensation of benzaldehyde with acetone (Fig. 9). This suggests that both reactions proceed at the same sites, and thus that both isomerization and aldolization occur by a basic mechanism.

## *Comparison of Different Solid Bases for Isophore Isomerization*

An attempt was made to check the use of this reaction with other solid bases and to investigate the effect of basic strength. We selected supported KF because it has been reported as a solid base (30, 31), a MgLa mixed oxide, and barium hexa-aluminate. Ba hexa-aluminate shows a layer structure with exposed Ba cations (32), which should introduce basicity and indeed Ba/alumina is used as a $NO_x$ trap for the purification of diesel exhausts in the Toyota process (33). The results are reported in Table 4 and show that the solid with the higher number of sites is hydrated HT-21. KFA and $BaAl_{12}O_{19}$ show a smaller number of sites compared to that of HT. The activation of KF1$\alpha$ at 723 or 923 K results in the same activity, showing a good stability of fluorine on the solid, as was also suggested by the results of thermal analysis. KFA is more active than KF1$\alpha$ supported by $\alpha$-alumina for this isomerization, which is in line with the much higher F loading on KFA. MgLa mixed oxides appear as solid bases of high basic strength since they are

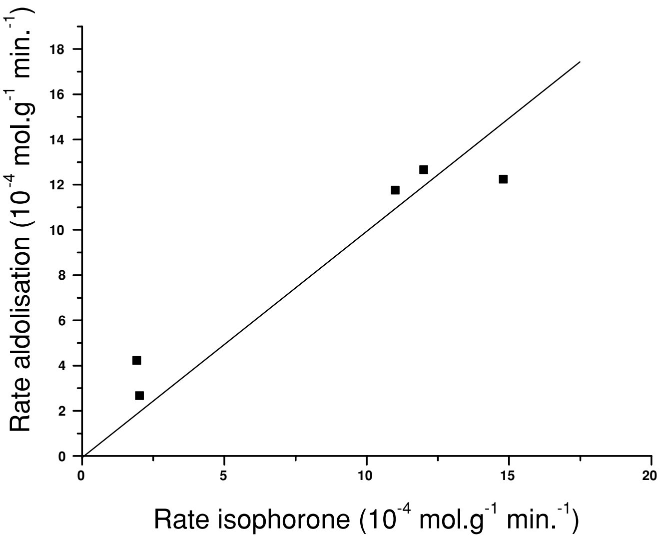

**FIG. 9.** Relationship between the rates of isophorone isomerization at 308 K and Claisen–Schmidt condensation at 273 K on MgAl samples rehydrated at room temperature.

### TABLE 4

### Activities of Different Solid Bases for the Isomerization of Isophorone

| Sample | Activation temperature (K) | Rate ($10^4$ mol/g/min) |
|---|---|---|
| HT-3 calcined | 723 | 9.3 |
| HT-21 R | 723, then rehydrated | 82 |
| MgLa-2 | 923 | 6 |
| MgLa-3 | 923 | 4 |
| MgLa-20 | 923 | 1 |
| KFA | 923 | 19 |
| KF1$\alpha$ | 723 | 0.7 |
| KF1$\alpha$ | 923 | 0.7 |
| $BaAl_{12}O_{19}$ | 923 | 12.4 |
| $BaAl_{12}O_{19}$ | 723 | 7.5 |

decarbonated at high temperature. Activity decreases with the concentration of La oxide on the solid, thus suggesting that the active sites are related to La.

A quantitative approach was attempted in the determination of the amount of $CO_2$ adsorption on these bases. The peaks of $CO_2$ were normalized to 1 g of sample and integrated to measure the amount lost by the solid. The activity of calcined samples plotted as a function of this integrated area is reported in Fig. 10. A good linear correlation is obtained, including for MgLa, BaAlO, and KF, showing the same behavior for these solids independent of strength. The point for HT-3 is slightly above, but since the rate is strongly affected by rehydration, this may be due to a not-complete dehydroxylation of the surface at 723 K.

In conclusion, the good agreement on the number of sites determined by $CO_2$ adsorption and the results of base-catalyzed reactions is satisfactory since it justifies this technique for basicity characterizations of surfaces. The comparison of several solid bases shows that hydrotalcite first decarbonated and then rehydrated is a mild base but possesses a large number of sites.

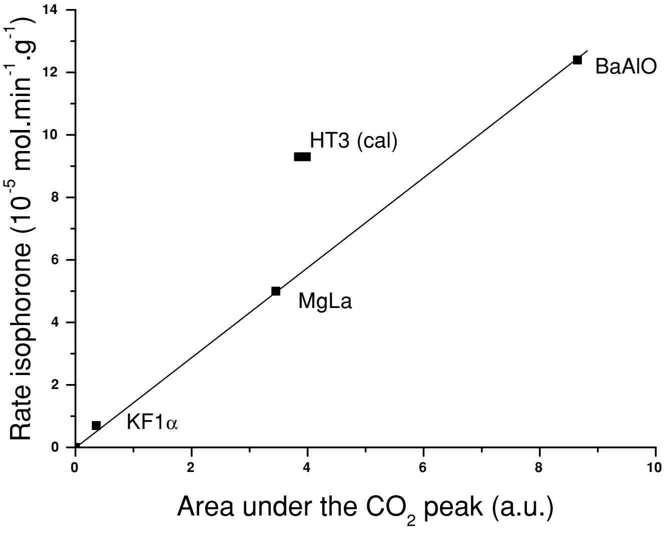

**FIG. 10.** Rate constant for isophorone isomerization at 308 K as a function of the number of sites determined by $CO_2$ adsorption for a series of basic samples.

## REFERENCES

1. Rey, F., Fornes, V., and Rojo, J. M., *J. Chem. Soc. Faraday Trans.* **88**, 2233 (1992).
2. Reichle, W. T., Kang, S. Y., and Everhardt, D. S., *J. Catal.* **101**, 352 (1986).
3. Brindley, G. W., and Kikkawa, S., *Clays Clay Miner.* **28**, 87 (1980).
4. Miyata, S., *Clays Clay Miner.* **23**, 369 (1975).
5. Cavani, F., Trifiro, F., and Vaccari, A., *Catal. Today* **11**, 173 (1991).
6. De Roy, A., Forano, C., El Malki, K., and Besse, J. P., *in* "Synthesis, of Microporous Materials" (M. L. Occelli and H. Robson, Eds.), Vol. 2, p. 108. Van Nostrand–Reinhold, New York, 1992.
7. Tichit, D., Lhouty, M. H., Guida, A., Chiche, B., Figueras, F., Auroux, A., and Garrone, E., *J. Catal.* **151**, 50 (1995).
8. Rao, K. K., Gravelle, M., Sanchez-Valente, J., and Figueras, F., *J. Catal.* **173**, 115 (1998).
9. Tessier, R., Tichit, D., Figueras, F., and Kervenal, J., French Patent 95 00094 (1995).
10. Cativiela, C., Figueras, F., Fraile, J. M., Garcia, J. I., and Mayoral, J. M., *Tetrahedron Lett.* **36**, 4125 (1995).
11. Climent, M. J., Corma, A., Iborra, S., and Primo, J., *J. Catal.* **151**, 60 (1995).
12. Kumbhar, P., Sanchez-Valente, J., Lopez, J., and Figueras, F., *Chem. Commun.* 535 (1998).
13. Corma, A., Iborra, S., Miquel, S., and Primo, J., *J. Catal.* **173**, 315 (1998); Spanish Patent 96 01087 (1996).
14. Velu, S., and Swamy, C. S., *Appl. Catal. A* **119**, 241 (1994).
15. Lopez, J., Jacquot, R., and Figueras, F., *Stud. Surf. Sci. Catal.* **130**, 491 (2000).
16. Guida, A., Lhouty, M. H., Tichit, D., Figueras, F., and Geneste, P., *Appl. Catal. A* **164**, 251 (1997).
17. Ai, M., *J. Catal.* **40**, 318 (1975).
18. Gervasini, A., and Auroux, A., *J. Catal.* **131**, 190 (1991).
19. Diez, V. K., Apesteguia, C. R., and Di Cosimo, J. I., *Catal. Today* **63**, 53 (2000).
20. Lauren-Pernot, H., Luck, F., and Popa, J. M., *Appl. Catal.* **78**, 213 (1991).
21. Aramendia, M. A., Borau,V., Garcia, I. M., Jimenez, C., Marinas, A., Marinas, J. M., Porras, A., and Urbano, F. J., *Appl. Catal.* **184**, 115 (1999).
22. Audry, F., Hoggan, P. E., Saussey, J., Lavalley, J. C., Lauron-Pernot, H., and Le Govic, A. M., *J. Catal.* **168**, 471 (1997).
23. Dessau, R. M., Zeolites **10**, 205 (1990).
24. Nosberger, P., U.S. Patent, 5,276,197 (1994).
25. Hutter, R., Mallat, T., Peterhans, A., and Baiker, A., *J. Mol. Catal. A* **138**, 241 (1999).
26. Miyata, S., *Clays Clay Miner.* **28**, 50 (1980).
27. Artizzu-Duart, P., Millet, J. M., Guilhaume, N., Garbowski, E., and Primet, M., *Catal. Today* **59**, 163 (2000).
28. Sanchez-Valente, J., Figueras, F., Gravelle, M., Lopez, J., and Besse, J.-P., *J. Catal.* **189**, 370 (2000).
29. Roelofs, J. C. A. A., van Dillen, A. J., and de Jong, K. P., *Catal. Today* **60**, 297 (2000).
30. Ando, T., Brown, S. J., Clark, J. H., Cork, D. G., Hanafusa, T., Ichihara, J., Miller, J. M., and Robertson, M. S., *J. Chem. Soc. Perkin Trans.* **2**, 1133 (1986).
31. Hattori, H., *Chem. Rev*. **95**, 537 (1995).
32. Wells, A. F., "Structural Inorganic Chemistry," 3rd ed. Oxford Univ. Press, Oxford, 1962.
33. Guyon, M., Blejean, F., Bert, C., and Le Faou, Ph., *Soc. Automot. Eng.* **SP-1399**, 87 (1998).