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Hydrogen Transfer Reduction of 4-*tert*-Butylcyclohexanone and Aldol Condensation of Benzaldehyde with Acetophenone on Basic Solids

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The liquid-phase reduction of 4-*tert*-butylcyclohexanone into 4-*tert*-butylcyclohexanol by reaction with isopropanol at 355 K has been studied on solid bases: mixed oxides obtained by calcination of hydrotalcites, NaBEA zeolites, KF/alumina, and La_2O_3 characterized by calorimetric FTIR adsorption of CO_2 and FTIR pyridine adsorption. The aldol condensation of benzaldehyde and acetophenone at 423 K was investigated in parallel to clarify the mechanism of deactivation. For hydrogen transfer, the addition of amine to the reaction medium had only a small effect, but benzoic acid strongly decreased the rate, suggesting catalysis by basic sites. Hydrotalcite was also active and selective for the hydrogenation of cinnamaldehyde into cinnamylalcohol. The stronger bases such as KF/alumina and La_2O_3 showed a low activity for hydrogen transfer, due to deactivation by the products of the parallel aldolization of the ketone. The exchange of BEA by Na^+ increased the selectivity to *cis*-alcohol with little effect on activity. NaBEA zeolites retained extraframework Al species of strong Lewis acidity and catalyzed the reduction of cinnamaldehyde into isopropyl-cinnamyl ether, thus suggesting an acidic mechanism in that case. © 2002 Elsevier Science (USA)

Key Words: **transfer hydrogenation; solid base; zeolite BEA; 4-*tert*-butylcyclohexanone; 4-*tert*-butylcyclohexanol; lanthanum oxide; potassium fluoride; hydrotalcite.**

INTRODUCTION

The chemo- and regioselective heterogeneous catalytic hydrogenation of unsaturated carbonyl compounds is an active research area (1). The hydrogenation of unsaturated aldehydes can lead to the formation of saturated aldehydes or unsaturated alcohols as primary products, which can be overhydrogenated to saturated alcohols. The most important product from an industrial point of view, and at the same time the most difficult to obtain, is the unsaturated alcohol (2). This reaction can be performed with hydrogen but the reduction by hydrogen transfer using hydrogen donors is also well-known and attractive because it avoids the use of high hydrogen pressure, which requires specific equipment (3).

The Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones is one such reaction where high selectivities are obtained using as catalyst metal alkoxides such as $Al(O{-}iPr)_3$ and $La(O{-}iPr)_3$ (4). However, the metal alkoxide catalysts are homogeneous, create problems in separation, and are not reusable. Hence, reusable heterogeneous catalysts will have a distinct advantage if they can match the performance of homogeneous catalysts. In this regard Posner *et al.* (5) reported the use of Al_2O_3 as catalyst. However, the activity was low and a large amount of catalyst was needed (1–2 g of Al_2O_3/mmol substrate) to achieve high conversions.

Recently, Creyghton *et al.* (6, 7) showed that properly activated zeolite H-β was a highly active and stereoselective catalyst for the reduction of 4-*tert*-butylcyclohexanone to *cis* 4-*tert*-butylcyclohexanol. The mechanism involved Lewis acid sites described as Al species partially attached to the lattice (8). The *cis*–*trans* selectivity could be tuned by partial exchange of the protons ($M/Al = 0.4$–0.6) by alkaline cations. This stereoselectivity was explained by a transition state selectivity imposed by the zeolite structure, and the effect of cation exchange was depicted as a fine-tuning of the internal porosity of the zeolite to favor this selectivity.

For alkaline zeolites, MgO, and KOH/alumina, Berkani *et al.* (9) reported that in the gas-phase reduction of cyclohexanone by cyclopentanol, the activity decreased upon CO_2 addition, therefore showing that hydrogen transfer proceeds at basic sites. Kaspar *et al.* (10) have reported the use of MgO as a moderately selective catalyst for the reduction of α,β-unsaturated ketones in a fixed-bed reactor in the vapor phase. Szöllösi and Bartók (11) observed a stabilization by treatment with carbon tetrachloride of the activity of MgO in transfer hydrogenation of ketones performed at about 523 K in the gas phase. This effect was attributed to the formation of acidic OH groups, which would activate the ketone (12). Earlier Niyama and Echigoya (13) reported that catalysts having adequate acidity and basicity show high activity for this reaction, and Ivanov *et al.* (14) reported that MPV reductions can be catalyzed by both basic and acid sites.

Drawbacks of an acid-catalyzed process are the possibility of dehydration of the alcohol with formation of

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ethers and olefins and fast aldolization of aldehydes by acid catalysis. We reported earlier that the catalytic transfer hydrogenation between isopropyl alcohol and 4-*tert*-butylcyclohexanone or unsaturated aldehydes to the corresponding unsaturated alcohol could be catalyzed in the liquid phase at 353 K by the mixed oxides derived from hydrotalcites (15). The process has now been generalized to the hydrogenation of benzaldehyde with several alcohols (16), of citral (17, 18), of aryl alkyl ketones (19), and of propiophenone (20). The mechanism of this hydrogen transfer reaction is not clear, however, especially concerning the respective role of acid and basic sites since the mixed oxides also show some acidity, illustrated for instance by the formation of mesityloxide in the aldolization of acetone (21).

We report here complementary data on the liquid-phase reaction catalyzed by mixed oxides using selective poisoning of the surface sites and the comparison of solids of known basicity. This hydrogen transfer reaction has been investigated on solid bases using the conversion of 4-*tert*-butylcyclohexanone and of cinnamaldehyde. The parallel reaction of aldolization, very fast with aldehydes, was investigated separately using the condensation of benzaldehyde on acetophenone.

EXPERIMENTAL

Materials

We used hydrotalcites (HDT) with different Mg/Al ratios, NaBEA zeolites, La_2O_3, and γ-Al_2O_3, either pure or modified by KF. The preparation of these solids was reported earlier (22, 23). HDT and La_2O_3 were prepared by precipitation at constant pH. KFA was a KF/alumina purchased from Aldrich. A sample referred to as KF10 was prepared with the same content of 10 mmol/g on a γ-alumina (SCP 350 from Procatalyse) with a surface area of 400 m^2/g. After calcination at 823 K the KFA sample shows a surface area of 14.9 m^2/g and KF10 of 9.7 m^2/g, so that the two samples are comparable.

Two samples of BEA from PQ Zeolites B.V. (CP 806 B25, Si/Al = 11.5 from the manufacturer, referred to as BEA-PQ) and Zeolist (P 811, given for Si/Al = 12.5, referred to as BEA-SC) were also used. The template was first calcined in air at 823 K (reached at 1 K/min). The two zeolites were then exchanged by Na, by dispersing 20 g of calcined zeolite in 1 L of a 0.1 M solution of Na acetate. Two successive exchanges were performed, then the solid was washed with water and dried at 353 K. The exchanged solids are denominated NaBEA-PQ and NaBEA-SC.

These solids were characterized by XRD on a Siemens D500 instrument, by measurement of surface area and porosity using a computer-driven homemade apparatus, and for some of them by calorimetry, using CO_2 adsorption at room temperature with a SETARAM C80 calorimeter on samples activated in vacuum at 673 K.

The acido–basic properties and structure of BEA zeolites was investigated using FTIR spectroscopy using self-supported thin wafers, mounted in a vacuum cell, and a Bruker instrument with a 4-cm^{-1} optical resolution. The solid was first calcined *in situ* in oxygen, then evacuated at 773 K. The adsorptions of CO_2 and pyridine were investigated after desorption at different temperatures.

Catalytic Reactions

The hydrogen transfer reaction was investigated in the liquid phase at reflux of isopropanol (355 K) and substrate (0.158 g) was dissolved in 10 ml of isopropanol used both as solvent and as hydrogen donor. The catalyst (0.15 g) was previously calcined in a flow of air at 723 K for HDT and supported KF, 823 K for zeolites, and 923 K for La oxide and then cooled in dry nitrogen. Poisoning of HDT was investigated using water, di-isopropylamine, or benzoic acid added to the reaction medium.

The aldol condensation of benzaldehyde with acetone was investigated in a batch reactor at 273 K on hydrotalcites first calcined and then rehydrated. The reaction mixture consisted of 0.51 ml of benzaldehyde (5 mmol) in 11.85 ml of acetone (0.16 mol). The reaction yields the aldol (4-hydroxy,4-phenylbutan-2-one) as well as the unsaturated ketone (4-phenylbut-3-en-2-one) produced by dehydration. The initial selectivity is higher than 95% in aldol and decreases to 84% at 73% conversion of benzaldehyde on HT21 (see Table 1), so that the initial rate is characteristic of pure aldolization.

The aldol condensation of benzaldehyde with acetophenone was investigated in the liquid phase using a batch reactor at 423 K with a reaction mixture consisting of 0.89 ml of acetophenone and 0.76 ml of benzaldehyde dissolved in 6.4 ml of dimethylformamide (DMF) as solvent. The main product of the reaction was the chalcone (1,3-diphenyl-2-propen-1-one) formed on hydrotalcite with a selectivity higher than 99%. Some catalysts also formed 1,3,5-triphenylpentan-1,5-dione, the product of Michael addition

TABLE 1

Composition and Texture of the Oxides after Activation at 723 K for HDTs and Supported KF, 823 K for Supported KNO_3, and 923 K for La Oxide

Solid	Mg/Al ratio	S_{BET} (m^2/g)	Total pore volume (ml/g)
HT5	2.23	254	0.71
HT6	1.82	260	0.40
HT13	2.93	276	0.74
HT14	3.90	280	0.63
HT15	4.85	310	0.75
HT21	1.95	197	0.52
La_2O_3	—	12.4	0.05
KFA	—	14.9	0.05

of acetophenone on the chalcone identified by GC–MS coupling. The Michael reaction is usually considered to require a strong basicity and the occurrence of this reaction is taken as evidence of stronger basicity of the solid. For both aldolizations the weight of the sample was 0.15 g. The catalyst was first calcined at 723 K, cooled to room temperature, then rehydrated in a flow of nitrogen saturated with water. For the three reactions, reactants, and products were analyzed by gas chromatography using a DB5 capillary column (25 m × 0.32 mm) and a Perkin–Elmer Autosystem.

RESULTS

Characterization of the Catalysts

It is well-known that the HDT structure exists only in a restricted range of compositions (24, 25). The *a* parameters of the different hydrotalcites used here obey Vegard's law as a function of the concentration of Al, suggesting isomorphic substitution of Mg by Al (Fig. 1). After calcination at 723 K the HDT structure is lost and a solid solution of MgO structure is formed. The surface areas of the different solids are reported in Tables 1 and 2 with the chemical compositions. All nonzeolitic solids are mesoporous and show an average pore size of about 3 nm.

The thermogram representative of the basicity of three representative samples, measured by the adsorption of CO_2, is presented in Fig. 2. The different HDTs show similar initial heats of adsorption with quite different numbers of sites. KF10 shows a slightly lower initial heat of adsorption but a number of sites comparable to that of HDT. La oxide was reported earlier to be a strong base with a large number of sites (about 4 μmol/m^2) adsorbing CO_2 with a heat of 120–150 kJ/mol (26). La_2O_3 is therefore more basic than HDT or KF.

NaBEA is expected to be a weak base (27) and its acid–base properties were investigated by FTIR spectrometry using the adsorption of CO_2 and pyridine at room temperature. Vimont *et al.* (28) and Kiricsi *et al.* (29) reported the presence of a band at 3782 cm^{-1} in the IR spectrum of HBEA calcined at 773 K. This band was assigned to a basic OH species attached to a tricoordinated Al atom. This Al atom is a Lewis site and the OH is the basic counterpart associated with this site. Indeed the spectrum of our NaHBEA sample shows the band at 3786 cm^{-1} after vacuum evacuation (Fig. 3). After introduction of CO_2 at room temperature and evacuation at 373 K for 30 min, the spectrum contains two small bands between 1500 and 1600 cm^{-1} and a narrow band at 3607 cm^{-1} assigned to hydrogeno carbonate (30). These bands disappear upon evacuation at 573 K.

NaBEA did not show the band at 3786 cm^{-1} after evacuation. A band that was observed at 3604 cm^{-1} in the presence of 30 Torr of CO_2, shifted to 3610 at 130 Torr of CO_2, and disappeared after room temperature desorption. Therefore the Al–OH species evidenced on HNaBEA does not exist on NaBEA. Two bands appear between 1600 and 1700 cm^{-1} in the carbonate region, which are still observed after evacuation in vacuum at 573 K. Decarbonation of hydrotalcite requires a temperature of 673 K; therefore the basicity of NaBEA is lower, but not negligible.

TABLE 2

Chemical Compositions of the BEA Zeolite Samples

Sample	% Al	% Na	Si/Al	Na/Al
NaHBEA-PQ	3.7	1.04	11.2	0.32
NaBEA-PQ	3.65	2.7	11.2	0.9
NaHBEA-SC	3.5	0.25	11.5	0.08
NaBEA-SC	3.5	1.9	11.6	0.6

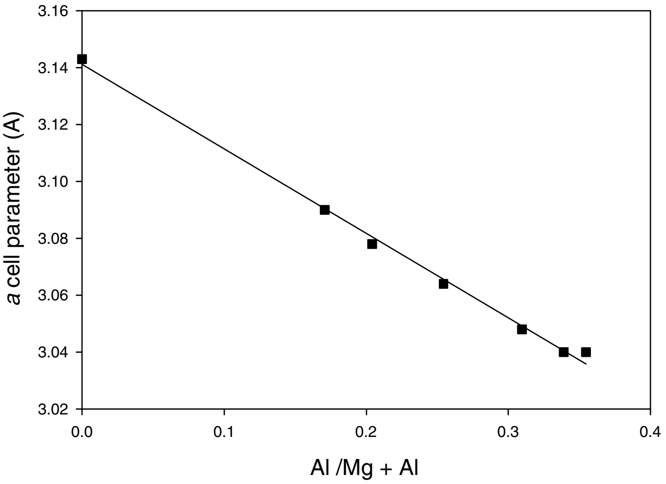


FIG. 1. *a* cell parameter of the different hydrotalcites.

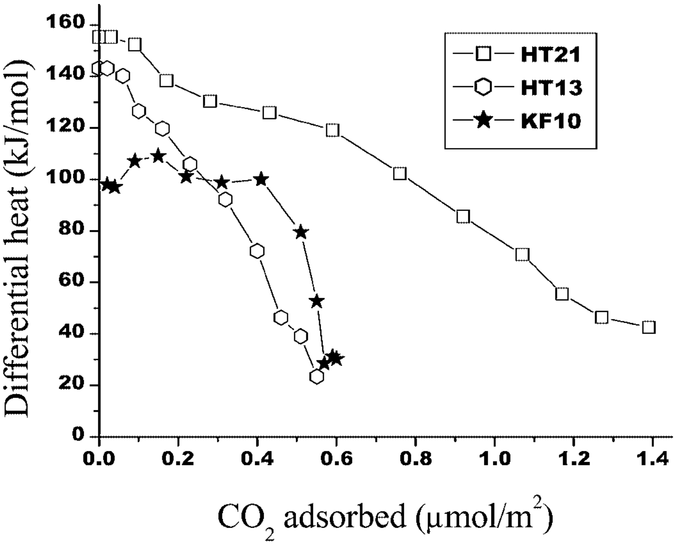


FIG. 2. Adsorption of CO_2: comparison of hydrotalcites and supported KF.

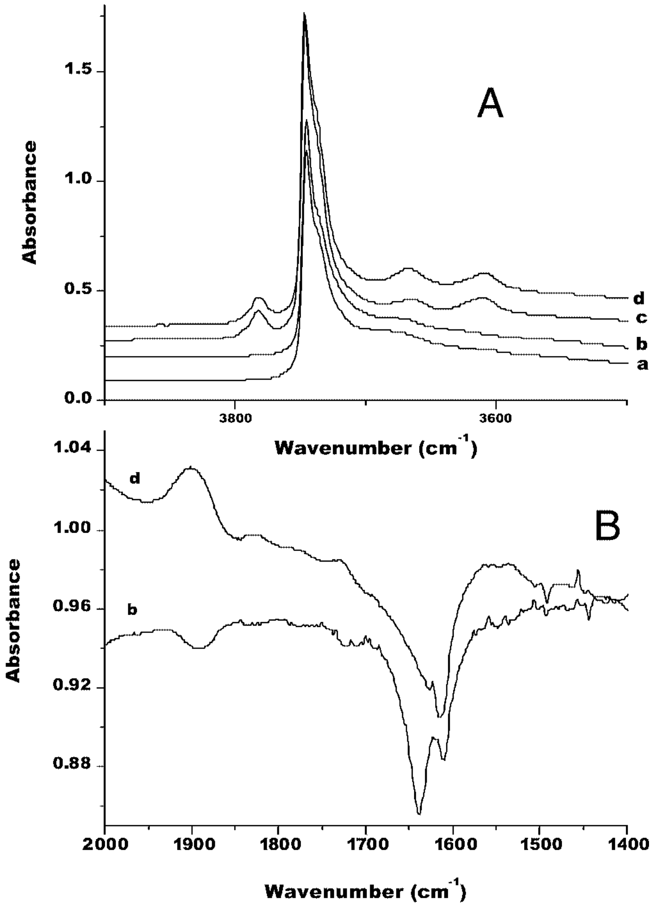


FIG. 3. Infrared spectra in the region of OH (A) and of carbonates (B) after vacuum evacuation at 773 K and after adsorption CO_2 (15 Torr) and further desorption at 373 K of BEA-SC zeolites: (a) NaBEA, (b) NaBEA–CO_2, (c) NaHBEA, and (d) NaHBEA–CO_2.

The FTIR spectra recorded after pyridine adsorption at room temperature and subsequent evacuation at 423 K for 1 h are reported in Fig. 4A. Both Lewis and Brønsted acid sites exist on the original samples after calcination, and as expected Brønsted acidity disappears by cationic exchange. Two bands are observed in the region corresponding to pyridine coordinated to Lewis sites: a band between 1450 and 1460 cm^{-1}, assigned to adsorption on an Al^{3+} site, and a second one, at 1444 cm^{-1}, and more intense on the solids containing sodium, which has been assigned to adsorption on Na^+ (31). After desorption at 573 K (Fig. 4B) the band at 1444 cm^{-1} is still clearly observed on the two samples in the Na form but with a lower intensity. However, the band at 1456 cm^{-1} characteristic of Lewis Al^{3+} sites is also observed in all cases. This site cannot be associated with the Al species partially attached to the lattice, characterized by the band at 3786 cm^{-1} observed on the protonic samples only, and is therefore attributed to extra framework Al. Cationic exchange by Na^+ therefore reduces, but does not eliminate, all extra framework species responsible for this strong acidity.

MVP Hydrogenation

We first checked the conditions of activation. The initial rate of reaction equal to 0.85×10^{-4} mol/min · g observed after activation at 623 K goes though a maximum at 4.1×10^{-4} mol/min · g after activation at 723 K, then decreases to 2.2×10^{-4} mol/min · g after activation at 823 K. If the sample activated at 723 K is rehydrated in N_2 saturated with water, as used for aldolization, no reaction takes place. Water is therefore a poison for the hydrogen transfer reaction. The

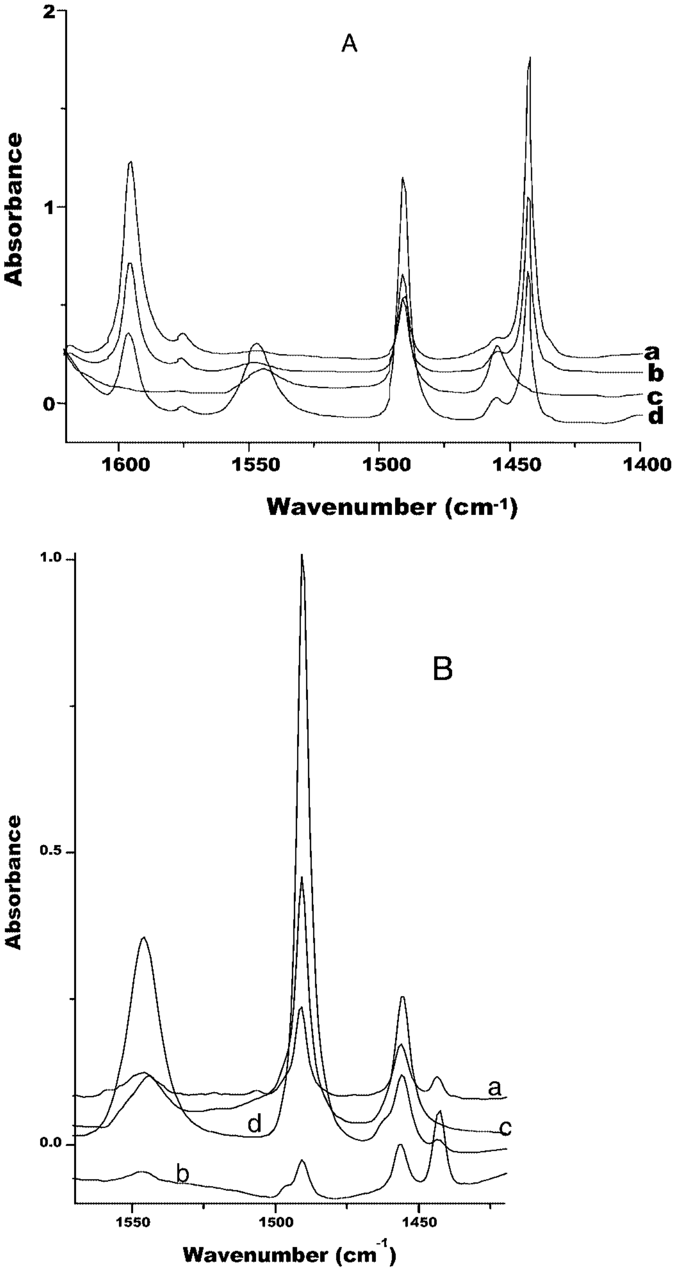


FIG. 4. Infrared spectra of pyridine after desorption at 423 K (A) and 573 K (B), on (a) NaBEA–SC, (b) NaBEA–PQ, (c) NaHBEA–SC, and (d) NaHBEA–PQ.

TABLE 3

Effect of Poisons on the Rate and Selectivity of the Hydrogen Transfer Reaction after 15 min at 355 K

Catalyst	Conversion (%)	Selectivity to *cis* alcohol (%)
HT21	14.6	15.1
HT21 + 35 μl di-isopropylamine	10.9	15.9
HT21 + 30 mg benzoic acid	0.4	11.4

decrease of activity by calcination at 823 K is attributed to a partial sintering of the solid, as reported earlier (32).

To clarify the role of basic and acid sites, selective poisoning was used. For this purpose a small amount of poison, representing about 0.5 mol/mol of Al in the catalyst, was added to the solvent before the addition of the calcined solid. The reaction was then performed as usual. The results obtained after 15 min, which can be considered as the initial rate, are reported in Table 3. The addition of a base had only a small effect on rate, but benzoic acid dramatically inhibited the reaction. However, neither of the additives had a significant influence on the selectivity to *cis*-alcohol, which remained low.

The results of the progressive poisoning of basic sites are illustrated in Fig. 5. An irreversible deactivation should result in a linear decrease which is observed in the very initial part only, corresponding to about 0.2 mmol/g. The results can be described by a Langmuir–Hinshelwood law assuming a competition of adsorption between the alcohol and benzoic acid for the same sites. Since the mechanism involves the adsorption of isopropanol, this rate law can be written

$$R = k\lambda\mathrm{i}C\mathrm{i}/(1 + \lambda\mathrm{i}C\mathrm{i} + \lambda\mathrm{b}C\mathrm{b}),$$

where k is the rate constant and λi, Ci, λb, and Cb are the adsorption coefficients and concentrations of isopropanol and benzoic acid. For strong adsorptions as expected for benzoic acid, the equation can be simplified to

$$R = k\lambda\mathrm{i}C\mathrm{i}/(\lambda\mathrm{i}C\mathrm{i} + \lambda\mathrm{b}C\mathrm{b}).$$

This equation reduced to $R = k/(1 + \lambda\mathrm{b}C\mathrm{b}/\lambda\mathrm{i}C\mathrm{i})$ is fitted with a correlation coefficient $R = 0.9968$, as illustrated in Fig. 5. The rate constant thus obtained is $k = 1 \times 10^{-6}$ mol/s and the ratio $\lambda\mathrm{b}/\lambda\mathrm{i}C\mathrm{i} = 6365$; therefore $\lambda\mathrm{b}/\lambda\mathrm{i} = 860$. As expected the strength of adsorption of benzoic acid is higher than that of isopropanol, but competitive adsorption is possible because the large difference in adsorption coefficients is compensated for by the much higher concentration of isopropanol used as solvent.

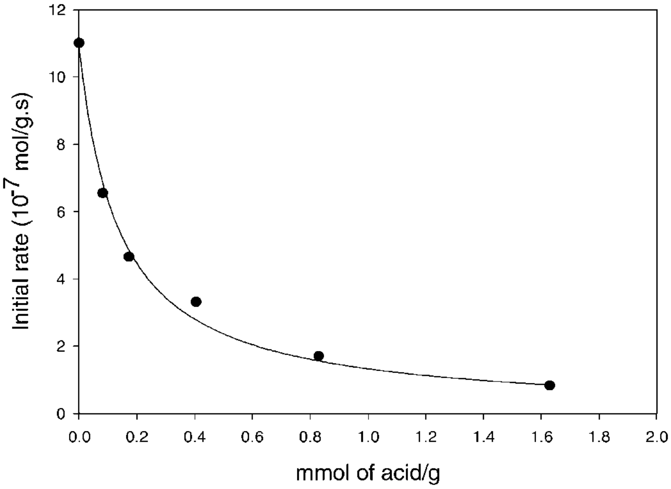


FIG. 5. Influence of the addition of benzoic acid to the initial rate of hydrogen transfer catalyzed by hydrotalcite at 355 K. The curve is the fit of the experimental points by a function $R = k/(1 + \lambda\mathrm{b}C\mathrm{b}/\lambda\mathrm{i}C\mathrm{i})$.

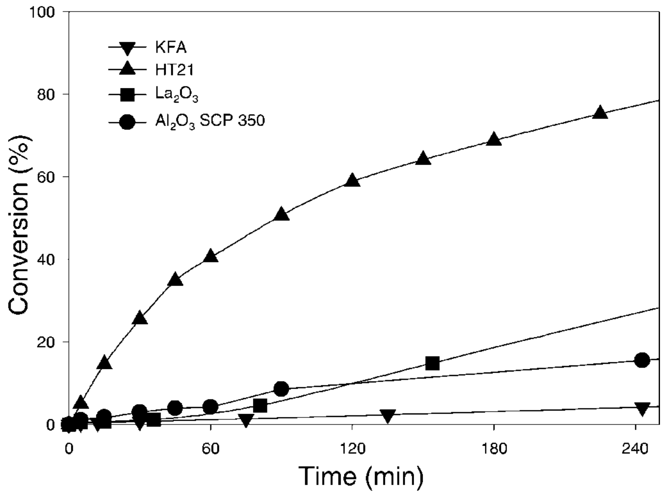


FIG. 6. Comparison of different solid bases for Meerwein–Ponndorff–Verley hydrogenation at 355 K.

The comparison of different HDTs is reported in Table 4 for solids showing Mg/Al ratios in the range 1.8–4.8. A

TABLE 4

Comparison of the Initial Hydrogen Transfer Rates on Hydrotalcites of Different Mg/Al Ratios

Solid (Mg/Al)	Initial reaction rate benzaldehyde + acetone ($\times 10^6$ mol $\cdot$ g^{-1} $\cdot$ s^{-1})	Initial rate for MVP ($\times 10^7$ mol $\cdot$ g^{-1} $\cdot$ s^{-1})	% *cis*
HT5 (2.2)	19.6	9.8	14.6
HT6 (1.8)	7	6.4	15.8
HT13 (2.9)	28.3	8.6	11.7
HT14 (3.9)	20.4	3	11
HT15 (4.85)	21.1	3.1	11.3
HT21 (2) (10°C/min)	35.5	11	15.1
HT21 (2) (1°C/min)		15	16.1

Note. Hydrogen transfer measured at 355 K on calcined samples and aldol condensation at 298 K on samples first calcined, then rehydrated.

TABLE 5

Comparison of the Catalytic Properties of BEA Zeolites at 355 K

Solid	NaBEA-PQ	NaHBEA-PQ	NaBEA-SC	NaHBEA-SC
Conversion at 10 min (%)	11.3	21.6	94.5	99.7
cis select. at 10 min (%)	95.1	95.4	98.5	96.0
Conversion at 6 h (%)	57.3	68.8	99.9	100
cis select. at 6 h (%)	98.7	96.0	98.6	96.1

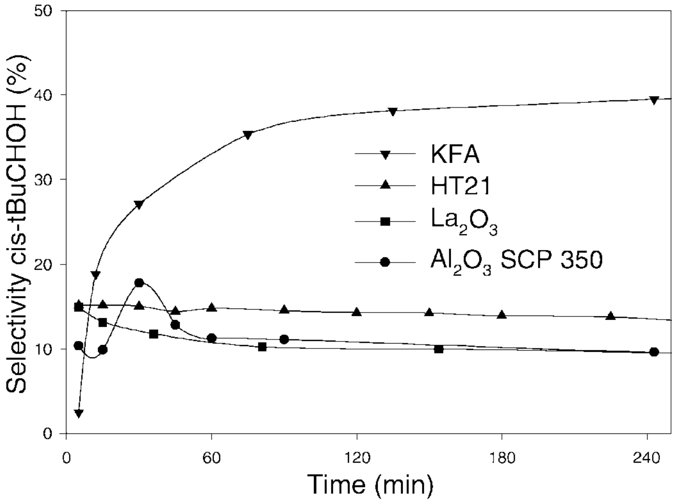


FIG. 7. Selectivity to *cis-t* butylcyclohexanone.

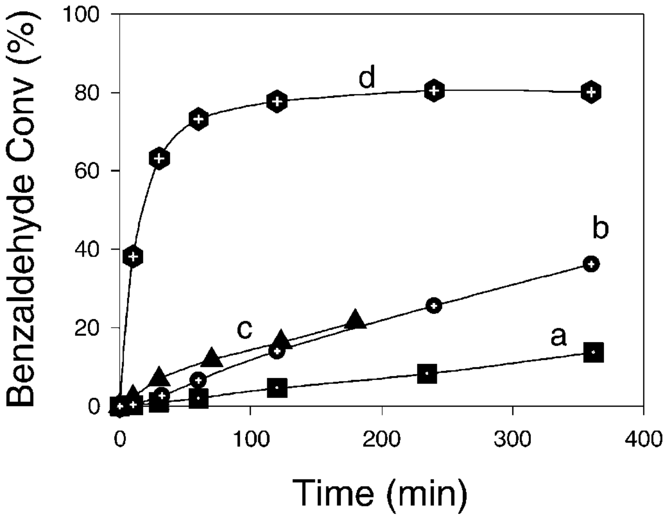


FIG. 8. Condensation of benzaldehyde on acetophenone at 423 K as a function of time for a series of solid bases: (a) calcined HDT, (b) La_2O_3, (c) HDT calcined then rehydrated, and (d) KF/Al_2O_3.

TABLE 6

MVP Reduction of Cinnamaldehyde at 355 K on MgAl Mixed Oxides and BEA Zeolites

Sample	Time (h)	Conversion (%)	Selectivity to unsaturated alcohol (%)
MgAl mixed oxide	5	75	92
NaBEA	5	12	55
NaHBEA	3	80	20[a]

[a] Main product: isopropyl-cinnamyl ether.

maximum of activity appears at about Mg/Al = 2. The effect of the heating rate in the calcination step was also investigated in order to check the possibility of decomposition of the sample by self-steaming. Changing this rate from 1 to 10 K/min did not greatly influence the rate or the selectivity to the *cis* isomer.

A comparison was also made with different bases, including KF/Al_2O_3 and La oxide. The results for some mesoporous solid bases are reported in Fig. 6 and those for BEA zeolites in Table 5. Among the nonzeolitic catalysts, the most active is the mixed oxide, showing a low selectivity to the *cis*-alcohol. Supported KF has a low activity but a relatively high *cis* selectivity (Fig. 7). The comparison of the MVP reduction of cinnamaldehyde on BEA and HDT is reported in Table 6. A significant difference appears in this reaction since NaBEA shows a low activity and NaHBEA a low selectivity with formation of isopropyl ether.

Aldol Condensation on Basic Catalysts

The same series of HDTs shows, after rehydration, a maximum in the rate of aldol condensation of benzaldehyde on acetone at a ratio of Mg/Al = 3 (Table 4). Earlier work showed that the heat of adsorption of CO_2 was comparable on calcined and rehydrated HDTs (22) and it is supposed that the basic strength is not dramatically altered by hydration. Therefore the lattice composition affects the two reactions slightly differently. It has to be remarked, however, that aldolization is suppressed by calcination on HDT. The results of Fig. 8 illustrate that high conversions can be reached with KF supported on Al_2O_3, and that La oxide is less active in this reaction.

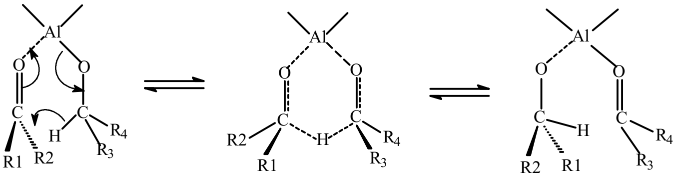
DISCUSSION

The activity of the mixed HDT oxides is clearly poisoned by acid and not by basic additives, therefore a basic mechanism has to be considered. The low activity of the stronger bases has, however, to be explained. It was reported earlier that after activation at high temperature, KF on alumina or La_2O_3, which show low activity in the present reactions, were active for the aldol condensation of benzaldehyde with acetophenone to chalcone at 423 K (Fig. 8) (23). The consecutive condensation of acetophenone on the chalcone by the Michael reaction was also observed, suggesting that rather strong basic sites are present. Their low activity may be related to this good activity for aldolization with formation of heavy products blocking the surface.

It is rather surprising that the exchange of protons on BEA zeolites shows such a small effect on activity. The NaBEA-PQ sample shows a lower activity with the same high selectivity. The reason for this cannot be diffusion limitations introduced by the larger particle size, since the rate (about 10^{-5} mol/s · g) is not very high. Indeed the zeolites activated at 723 K are surprisingly more active than those described by Creyghton *et al.* (7) since they reach nearly quantitative conversion to *cis*-alcohol in 10 min, compared to the 32% yield in 6 h reported by the previous authors. These authors observed high activities after calcination at 973 K or after mild steaming at 823 K. In both cases Lewis acidity is promoted at the expense of Brønsted acidity (33).

The conclusion of this present work is that cation exchange of BEA by Na^+ significantly reduces the global acidity, estimated after desorption at 423 K (Fig. 4A), but has a less marked effect on the stronger sites, retaining pyridine at 573 K (Fig. 4B). These sites are present in a small number only, but the intensities of the IR bands at 1456 cm^{-1} are roughly correlated with the observed activity. Indeed Creyghton *et al.* (7) reported that piperidine poisoned the activity, which demonstrates an acidic mechanism in that case.

The mixed oxides are, however, different since their activity is not poisoned by a strong base. The behavior for the hydrogen transfer hydrogenation of cinnamaldehyde is also different: NaHBEA forms ether, as expected for an acid mechanism, while the mixed oxides give cinnamic alcohol. The classic Al alkoxide intermediate proposed for the MVP reaction agrees with both acid or base mechanisms. The abstraction of a proton from isopropanol by a surface basic site should give an isopropoxide anion, stabilized at a Lewis Al site. This intermediate can undergo the process described in Scheme 1. In this mechanism acid sites are required to stabilize the anion, but the initial attack is due to a basic site in the case of the mixed oxides and to a proton in the case of BEA zeolites.



SCHEME 1. Mechanism for the Meerwein-Ponndorf-Verley hydrogenation with aluminium alkoxide.

In conclusion, selective poisoning of the surface sites of HDT suggests that the reaction is catalyzed by basic sites. This reaction path gives a much higher activity than previously reported, but the only solid which gives a high selectivity to the 4-*tert*-butylcyclohexanol is BEA zeolite. When this selectivity is not required, the mixed oxides derived from hydrotalcites are the best catalysts.

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