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Correlation between the basicity of solid bases and their catalytic activity towards the synthesis of unsymmetrical organic carbonates

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Abstract

The correlation between the basic properties of solid catalysts and the reaction rate of the selective synthesis of unsymmetrical organic carbonates via direct condensation of diethylcarbonate (DEC) and alcohols was investigated. A detailed kinetic study of the transesterification of 1-phenylethanol and DEC was made with catalysts with different basic strengths. The solids included fluorinated hydrotalcite, MgLa mixed oxides, CsF (pure or supported on α- and γ-aluminas), KF (pure or supported on α- and γ-aluminas), anatase, rutile, and zirconia. Basic properties were determined by the adsorption of CO_2, measured by gravimetry coupled with mass spectrometry and by calorimetry. Both techniques show a higher basicity for MgLa mixed oxides. The rate of the reaction was roughly proportional to the number of strongly basic sites present on the catalyst, except for CsF/α-Al_2O_3, which showed higher activity for several different substrates in spite of a lower number and strength of basic sites. This is attributed to the high nucleophilicity of the alcoholate formed as an intermediate. The addition of water to the reaction medium induces two effects: inhibition of the reaction and the promotion of etherification of the substrate by ethanol as a side reaction. The catalysts can be reused several times with a small loss of activity.

Keywords: Catalysis by solid bases; Transesterification; Alcohols; Basicity measurements; Kinetics; Unsymmetrical organic carbonates

1. Introduction

A major aim for the chemical technology of the future is the avoidance of noxious and environmentally unacceptable effluents, including salts and organic solvents [1–3]. Although solutions to this problem have been found in the case of acid catalysis, with more than 100 industrial processes operated in the world, much less success has been encountered for basic catalysis, with only a few processes [4]. Heterogeneous catalysis is particularly attractive because it allows the ready separation of the products from the catalyst. A particular example of this is organic carbonates, which are manufactured on a commercial scale and are used as intermediates in pharmaceuticals [5], plasticisers, synthetic lubricants [6], monomers for organic glasses [7], and solvents [8]. An environmentally benign preparation of alkyl carbonates from alkyl halides and alcohols in the presence of alkali metal carbonates or carbon dioxide has recently been developed [9–11] and paves the way to other synthetic methodologies. In homogeneous catalysis, unsymmetrical dialkyl carbonates are produced by transesterification of carboxylic acid diesters with an allyl alcohol in the presence of metal bases (inorganic carbonates, alcoholates, and hydroxides), with crown ethers or polyethylene glycols added as cocatalysts [12].

We recently reported MgLa mixed oxides [13] and CsF/α-Al_2O_3 [14] as new solid bases for the synthesis of the title compounds. These catalysts showed quite different behaviours: CsF/α-Al_2O_3 was more active and much less sensitive than MgLa mixed oxides towards the structure of the substrate. Here we attempt to establish a quantitative relation between the basic properties measured by the gravimetric and calorimetric adsorption of CO_2 and the catalytic activity for the transesterification of 1-phenylethanol and DEC,

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which was chosen as a model reaction in a solvent free system.

2. Experimental

2.1. Materials and methods

The solids included fluorinated hydrotalcite, MgLa mixed oxides, CsF (pure or supported on α- and γ-aluminas), KF (pure or supported on α- and γ-aluminas), CaF_2, anatase, rutile, and zirconia. α-Alumina (SPH 512, 10.5 m^2/g) and γ-alumina (SCP 350, 400 m^2/g) from Rhone Poulenc were used as supports. The samples supported by aluminas or titanias were prepared by aqueous impregnation of the commercial support with 1 mmol/g of fluoride. HDT-F was obtained by anionic exchange of hydrotalcite in the OH form in an aqueous solution of KF [15,16] and MgLa mixed oxide (Mg/La in the solid $= 4.26$) by coprecipitation from a solution of corresponding nitrates [17,18]. CsF/α-Al_2O_3, KF/α-Al_2O_3, HDT-F, and homogeneous analogues KF and CsF were activated by simple drying at 393 K for 4 h, and MgLa mixed oxide was calcined at 873 K for 5 h in air, and the remaining solids were treated under nitrogen at 673 K for 3–4 h prior to use.

The preparation of these solid bases has been reported previously [19,20], and their basicity has been measured in a qualitative form. A quantitative approach to basic properties is presented here, which measures the adsorption of CO_2 by microcalorimetry at room temperature. The instrument was a Calvet calorimeter coupled to a volumetric ramp [21]. The samples (0.1 g) were first evacuated at 673 K and then brought into contact with small doses of gas; the differential enthalpy of adsorption was then measured. This technique makes it possible to measure the number of sites of a given strength, evaluated by the enthalpy of adsorption. The results were checked by differential thermal gravimetry (DTG) performed with a Setaram DTA-DTG apparatus coupled with a mass spectrometer, which allowed us to measure the adsorption of carbon dioxide on the solid.

2.2. Catalytic reaction of 1-phenylethanol and DEC

An excess of DEC (33 mmol) and 1-phenylethanol (2 mmol) were placed in a three-necked round-bottomed flask equipped with a condenser. Freshly activated catalyst (0.1 g) was added, and the experiment was started with stirring in a nitrogen atmosphere at ~ 403 K with the addition of dodecane (0.05 ml) as an internal standard. Stirring was continued until the completion of the reaction as monitored by thin-layer chromatography. The composition of the reaction medium was analysed by gas chromatography with a Perkin–Elmer Autosystem equipped with a capillary column. The reaction selectively produces alkylcarbonate and ethanol. Because of its low boiling point, the ethanol is distilled during the reaction. The conversion was determined from the variation in the concentration of alcohol. After completion of the reaction the reaction mixture was filtered and the catalyst was washed with DEC (2×2.5 ml) to wash off the product adhering to the surface of the catalyst. The combined filtrate fractions were concentrated under reduced pressure to obtain a clean product. Excess DEC removed from the reaction mixture can be recycled for subsequent use. The product was analysed by ^1H and ^{13}C NMR, and the purity and structure of the product were confirmed by GC-MS analysis.

2.3. Recycling experiments

The reuse of the catalyst was investigated with MgLa mixed oxides and KF and CsF on α-Al_2O_3, with the use of 1-phenylethanol and 4-chloro-*sec*-phenylethanol as substrates. The reaction mixture was taken out with a syringe equipped with a microfilter after completion of the reaction, leaving the catalyst in the lowest possible amount of liquid, and then a new charge of reactants was added.

3. Results and discussion

3.1. Characterisation and basic properties of the solids

The surface areas of different catalysts are reported in Table 1; the homogeneous analogues (pure KF and pure CsF) were not evaluated because of their low surface area. Large differences in surface area are due to the choice of the support, since most often the acidity of the support changes

Table 1
Catalytic properties of various solid bases and of their homogeneous analogues in direct condensation of *sec*-phenethyl alcohol with DEC: A model reaction for the evaluation of the best catalyst[a]

Catalyst	Surface area ($m^2\,g^{-1}$)	Number of basic sites ($\mu mol\,g^{-1}$)	Reaction time (h)	Yield (%)[b]
CsF/α-Al_2O_3	7	11.4	0.45	100
KF/α-Al_2O_3	9.4	14	5.0	100
CsF/γ-Al_2O_3	217	–	12	57[b]
KF/γ-Al_2O_3	234	98	12	36[b]
HDT-F	–	47.7	12	100
KF/TiO_2 (Rutile)	6	–	12	88[c]
KF/TiO_2 (Anatase)	44	–	12	8[c]
KF/ZrO_2	–	–	12	44[c]
KF/CaF_2 (20 wt%)	–	–	12	12[c]
Pure KF	–	–	12	< 5[c]
Pure CsF	–	–	12	100
Mg La mixed oxide	37.6	14.9	3.5	100
Pure α-Al_2O_3	10.5	–	12	NR[e]
Blank[d]	–	–	12	NR

[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC and 0.1 g of catalyst in nitrogen atmosphere at 403 K.

[b] Yields are calculated with ^1H NMR and GC.

[c] Remaining is the starting material.

[d] In absence of catalyst.

[e] NR represents no reaction.

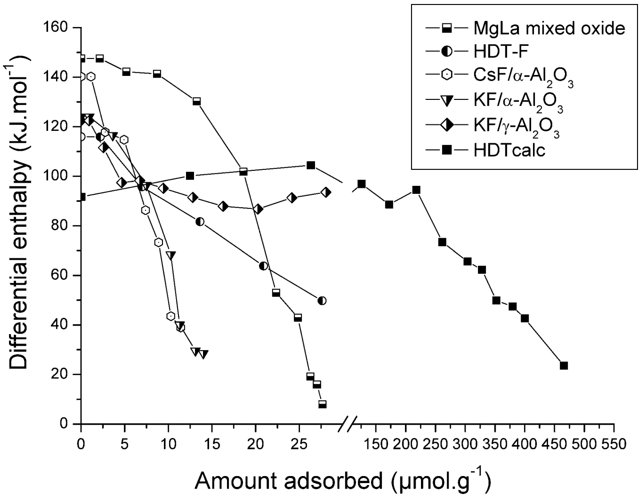


Fig. 1. Differential heats of adsorption of CO_2 on solid bases.

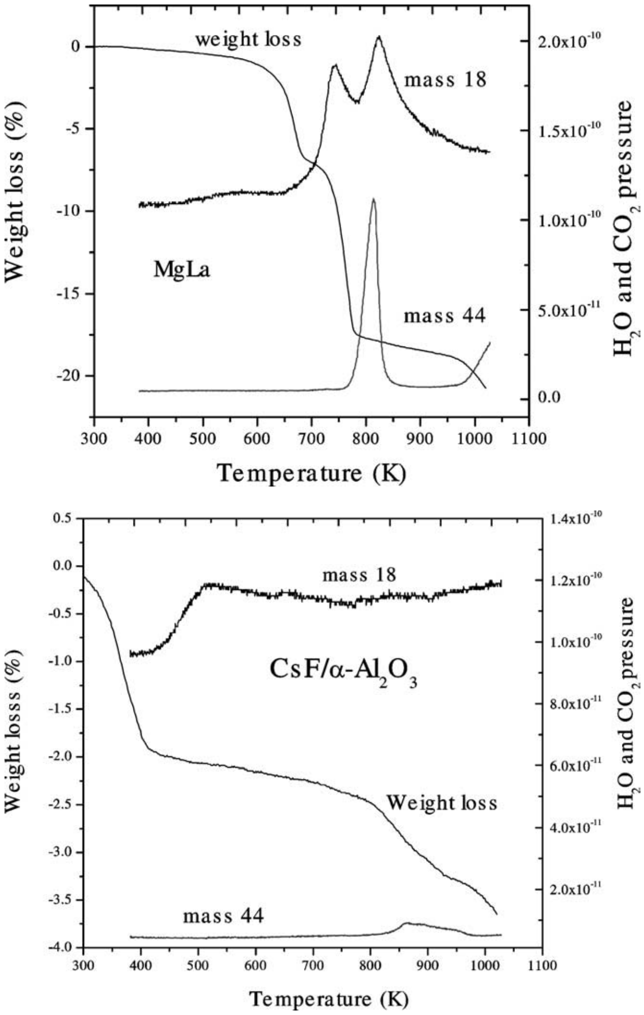


Fig. 2. Differential thermal gravimetric studies of MgLa and CsF/α-Al_2O_3.

with its surface area, which also controls the basic properties. MgLa mixed oxides, such as the fluorides supported by α-Al_2O_3 or titanias, show low surface areas and are nonporous.

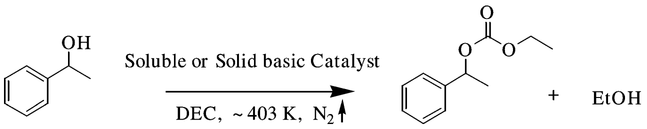
The basic properties of KF supported by α- or γ-alumina have been reported recently [20], and the calorimetric results are compared here with those for HDT, HDT-F, CsF/α-Al_2O_3, and MgLa mixed oxides (Fig. 1). CsF/α-Al_2O_3 showed a strong initial enthalpy of adsorption, with only a few basic sites. The distribution of basic sites of KF/α-Al_2O_3 is very close to that of CsF/α-Al_2O_3, with a lower initial enthalpy. KF/γ-Al_2O_3 showed a weaker basic strength and a larger number of basic sites. This lower basicity of KF/γ-Al_2O_3 has been attributed to the loss of KF due to its reaction with the support with the formation of fluoroaluminate, as detected by X-ray diffraction and solid-state ^{19}F-NMR spectroscopy [20]. A similar phenomenon has been observed for CsF, which partly retains its integrity on α-Al_2O_3 but disappears in reaction with the support on γ-Al_2O_3 [14]. The high basicity of CsF and KF on α-Al_2O_3 is then attributed to a good dispersion of the fluoride at the surface of an inert support, which makes it possible to preserve part of the original fluoride. If hydrotalcite appears as a weak base in this context, HDT-F is comparable to supported fluorides, showing a weaker initial heat of adsorption and a larger number of basic sites.

The higher basic strength was observed for MgLa mixed oxides with a lower number of basic sites. Pure La oxide is known to be a strong base, on which CO_2 is adsorbed with an initial heat of adsorption of about 140 $kJ\,mol^{-1}$ up to a coverage of 26 $\mu mol\,g^{-1}$. For higher coverages the heat of adsorption decreases fast and falls to 100 $kJ\,mol^{-1}$ at about 50 $\mu mol\,g^{-1}$ [22]. The MgLa mixed oxide shows an initial heat of adsorption close to 150 $kJ\,mol^{-1}$, which also decreases fast for a coverage above 20 $\mu mol\,g^{-1}$. The XRD pattern shows the presence of La oxide [18], and this catalyst therefore behaves like a pure La oxide, with a higher thermal stability of the surface area.

The basicity was also estimated by measuring the degree of carbonation of the solids by differential gravimetry. The results are reported in Fig. 2 for MgLa and CsF/α-Al_2O_3, where the intensities of the signal of the mass spectrometer have been normalised to the mass of sample in order to make a quantitative comparison. The two solids show similar behaviours in DTG, with the occurrence of two steps involving both dehydration and decarbonation. MgLa and CsF both exhibit a peak for CO_2 above 800 K, but the peak relative to MgLa is intense and that relative to CsF/α-Al_2O_3 is very small. These results of DTG analysis of decarbonation therefore confirm the results of calorimetry, pointing to greater basicity of the MgLa mixed oxide.

3.2. *Reaction kinetics*

We investigated the influence of both the number and strength of basic sites on the transesterification of DEC by 1-phenylethanol as a model reaction (Scheme 1).



Scheme 1. Model reaction for the synthesis of nonsymmetrical organic carbonates from an alcohol and DEC.

Table 2
Synthesis of carbonates from alcohols using MgLa mixed oxide, $CsF/\alpha\text{-}Al_2O_3$ and $KF/\alpha\text{-}Al_2O_3$ as catalyst using the standard conditions

Alcohol	Reaction time		
	MgLa	$CsF/\alpha\text{-}Al_2O_3$	$KF/\alpha\text{-}Al_2O_3$
Phenylethanol	6 h	30 min	
Sec-Phenethyl alcohol	4 h	20 min	5 h
Ethyl-1-(4-chloro) phenethyl alcohol	3.5 h	20 min	7 h
(+) Menthol	45 min	15 min	
Ethyl tetrahydrofurfuryl alcohol	4 h	30 min	

A first determination of catalytic properties was made by measurement of the time required to reach a reasonably high conversion of 1-phenylethanol, as illustrated in Tables 1 and 2. On this basis it was observed that pure KF was practically inactive, as were $\alpha\text{-}Al_2O_3$, KF on CaF_2, ZrO_2, and anatase. KF/rutile showed high activity and selectivity towards the desired product, as observed earlier in a Michael addition reaction [20]. Pure CsF catalyses the reaction but requires 12 h to reach full conversion, whereas $CsF/\alpha\text{-}Al_2O_3$ achieves this in 45 min, showing a much higher basicity. If we take into account the number of basic sites of these solid bases (Table 1), $CsF/\alpha\text{-}Al_2O$ converts 2 mmol of substrate to the corresponding product with about 1 µmol of active basic sites, and then reaches turnovers of 2000; and the MgLa mixed oxide achieves turnovers of 1300. Therefore it can be concluded that the reaction is catalytic.

It appeared at this stage that MgLa mixed oxides with a higher number of basic sites of higher strength showed poorer catalytic properties than $CsF/\alpha\text{-}Al_2O_3$ of lower basicity. This behaviour is not particular to one reaction but was confirmed on several substrates (Table 2) that reacted very fast on this catalyst: a quantitative conversion was observed typically in less than 30 min on $CsF/\alpha\text{-}Al_2O_3$, whereas the same result required hours with the MgLa mixed oxide. Similarly, the small differences in basicity between CsF and KF on α-alumina are not consistent with the large differences in reaction time. Therefore, a kinetic study was done with selected catalysts to investigate the correlation between the reaction rate and the basic properties. The kinetic data for the reaction in excess of DEC (ratio alcohol/DEC = 15) over most catalysts could be fitted well to a pseudo-first-order rate law:

$$\log(1/(1-x)) = (k_a/2.303)t,$$

where k_a is the apparent first-order rate constant, x is the fractional conversion of alcohol, and t is the reaction time. A plot of $\log(1/(1-x))$ as a function of time gives a linear plot over a large range of alcohol conversions, as illustrated in Fig. 3 for catalysts showing quite different activities. The reaction rate constants k obtained from these results were compared with the basic properties of the corresponding catalysts (Fig. 4). Indeed, the catalytic activity is not correlated with the total number of basic sites. This can be accounted for by the fact that only those sites able to abstract a proton from the alcohol can play a catalytic role. The results of Table 1 show a low activity for KF/γ-alumina, which has an initial energy of adsorption of about 120 $kJ\,mol^{-1}$, suggesting that the minimum basic strength required for the abstraction of a proton from 1-phenylethanol corresponds to an enthalpy of CO_2 adsorption higher than 120 $kJ\,mol^{-1}$. The results were then replotted in Fig. 5, under the assumption that the active sites are those for which $\Delta H > 120\ kJ\,mol^{-1}$. A rough correlation does appear between the number of these sites and the reaction rate, but $CsF/\alpha\text{-}Al_2O_3$ falls well away from of the line, which merits a special discussion.

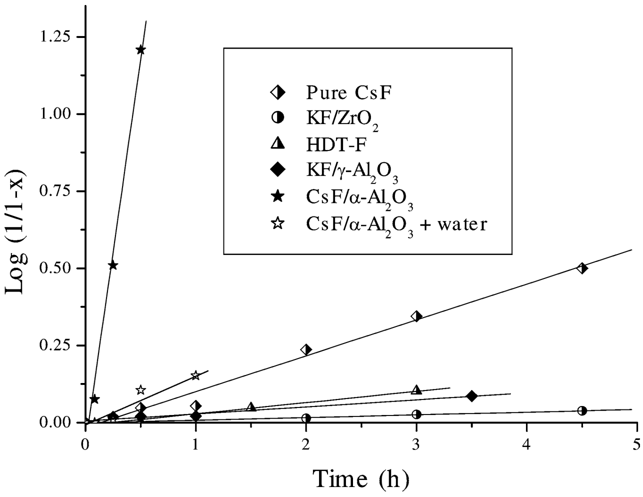


Fig. 3. First order plot of the conversion versus time on different catalysts, and effect of water on $CsF/\alpha\text{-}Al_2O_3$.

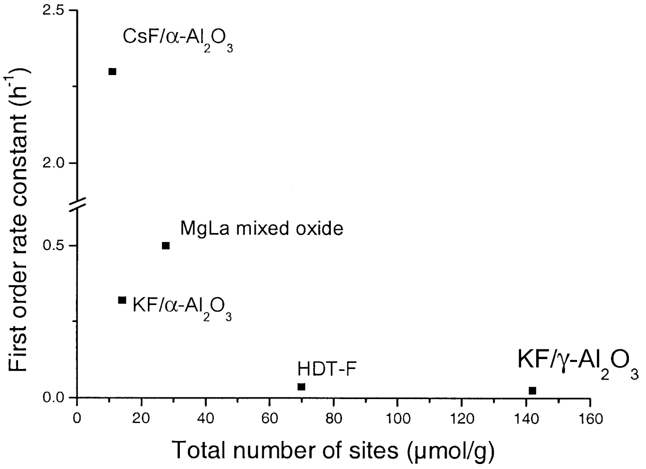


Fig. 4. Correlation of the reaction rate with the total number of active sites.

Because of the higher acidity of alcohols compared with DEC, the base-catalysed reaction most probably takes place

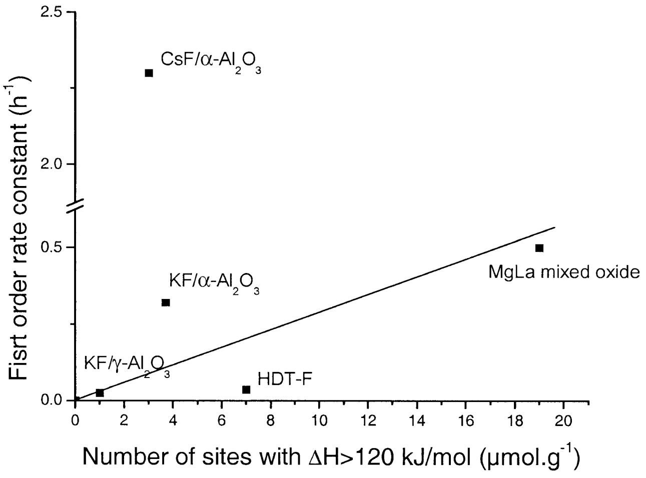


Fig. 5. Correlation between the reaction rate constant and the number of strong basic sites, adsorbing CO_2 with an enthalpy > 120 kJ mol^{-1}.

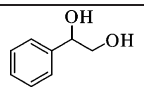
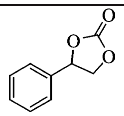
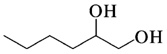
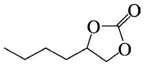
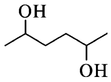
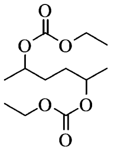
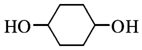
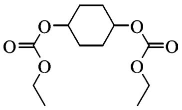
by proton abstraction by a negatively charged fluoride (or oxide) moiety to generate an alkoxide anion stabilised at the surface cation. The alkoxides conjugated with cesium are believed to constitute "naked anions" exhibiting enhanced nucleophilicity [5,23], and this mechanism accounts for the high activity of cesium fluoride and the low rate sensitivity towards the structure of the alcohol. In contrast, MgLa mixed oxides, even though they have comparable basicity, were found to show a rather strong sensitivity to the structure of the substrate. Weakly coordinated species should be more negatively charged, then reactive, and less sensitive to steric factors than an intermediate strongly bonded at the surface. Cs shows a Pauling radius of 1.69 Å compared with 1.33 Å for K, then a lower density of charge, accounting for the particular behaviour of this cation.

This low sensitivity of CsF/α-Al_2O_3 is particularly interesting for the fast and selective transesterification of 1,2-diols into cyclic carbonates (Table 3, entries 1 and 2), which are usually prepared from phosgene and carbodiimidazole [24] or bis(trichloromethyl) carbonate [25], whereas 2,5-hexanediol and 1,4-cyclohexanediol yielded the corresponding bis-carbonate as the sole reaction product (Table 3, entries 3 and 4). Therefore, this methodology permits us to offer a simple and efficient alternative to the existing methodologies. Another interesting observation was that the selectivity did not change with the conversion: according to the literature [5], in basic media the cyclic carbonates can undergo ring opening to give a mono-protected alcohol; this was not observed in our reaction conditions. The high selectivity towards the cyclic carbonate can be attributed to a lower rate of the secondary reaction or to the use of carbonate as solvent.

3.3. Recycling experiments

The reuse of the catalyst was investigated with MgLa mixed oxides and KF and CsF on α-Al_2O_3, with 1-phenylethanol and 4-chloro-*sec*-phenylethanol as substrates. As a general rule a lower activity is noticed in the second cycle, and the time required to reach complete conversion increases. From a practical point of view, however, a catalyst reaching a 97% yield in a slightly longer time can still be considered useful. With this criterion the catalyst can be recycled two times in the case of KF/α-Al_2O_3 and three times with CsF/α-Al_2O_3, with a longer reaction time required for the third cycle (Table 4). A chemical analysis of the cata-

Table 3
Synthesis of carbonates from diols using (a) MgLa mixed oxides and (b) CsF/α-Al_2O_3 as catalysts

Entry[a]	Alcohol	Reaction time	Product	Yield (%)[b]
1		(a) 2 h (b) 25 min		(a) 98 (b) 98
2		(a) 1 h (b) 20 min		(a) 97 (b) 97
3		(a) 45 min (b) 45 min		(a) 97 (b) 98
4		(a) 45 min (b) 30 min		(a) 98 (b) 97

[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC and 0.1 g of catalyst in nitrogen atmosphere at 403 K.

[b] Isolated yields.

Table 4
Reuse of various catalysts with two different substrates

Alcohol[a]	Experiment number	Reaction time (h)	Yield (%)[b]
CsF/α-Al_2O_3 as catalyst			
1-Phenylethanol	1	0.33	99
	2	0.5	98
	3	1.5	82
	4	12	14
4-Chloro-1-phenylethanol	1	0.41	98
	3	1.0	97
	4	12	21
MgLa mixed oxides as catalyst			
4-Chloro-1-phenylethanol	1	3.5	98
	2	4	97
	5	7	98
KF/α-Al_2O_3			
1-Phenylethanol	1	5	99
	2	7.5	98
	3	12	92
	4	12	16

[a] All the reactions performed on 2 mmol alcohol with 33 mmol of DEC in nitrogen atmosphere at 403 K.

[b] Isolated yields.

lysts used (after four cycles) revealed no loss of Cs, K, or F, and thus that the lower activity cannot be due to leaching. With MgLa mixed oxides, the situation is similar, with little change of activity after four recycles and a clear loss of activity after the fifth recycling only. The longer reaction time can be attributed to two main factors: some loss of catalyst remaining in suspension in the reaction mixture and inhibition by traces of water present in each new feed of reactants.

3.4. Inhibition effect of water on reaction kinetics

This hypothesis was checked by measurement of the kinetics in the presence of water (added initially at the level of 1 $\text{mmol}\,\text{mmol}^{-1}$ of alcohol). It was observed that water inhibits but does not completely suppress the reaction: the rate is very low for the reaction catalysed by $CsF/\alpha\text{-}Al_2O_3$ (Fig. 3), showing kinetic inhibition, but the yield after 1 h reached 57% with high selectivity. Up to this time, the kinetics was still first order and corresponded to a much lower rate constant. After this time, the ether corresponding to the alcohol, not detected in the absence of water, appeared as a by-product in large quantities (about 30%). With the MgLa mixed oxides, the same phenomenon was observed, with a yield reaching 52% after 2 h, followed by a slow rate with the appearance of ether as a by-product (20%). The formation of ether by reaction of diethylcarbonate with a diol, 1,4:3,6-dianhydrosorbitol, has been reported to be catalysed at 523 K by sodium methoxide or organic bases such as diazobicyclo[2,2,2]octane (DABCO) [26]. It was also observed earlier that in the absence of water in the reaction medium, esters were readily hydrolysed on hydrated hydrotalcites at about 323 K [27], a phenomenon not observed on dehydrated solids and therefore attributed to the presence of hydroxyls at the surface. Indeed, $CsF/\alpha\text{-}Al_2O_3$ is dehydrated in vacuum at about 400 K (Fig. 2) and readily rehydrated in air, and faster in water. A simple mechanism for the formation of ether by a base-catalysed reaction could be based on the following scheme, involving the hydrolysis of DEC, followed by decarboxylation of the anion to an alkoxide, which can react on the alcoholic substrate to form an ether:

$$\text{EtO–CO–OEt} + \text{OH}^- \rightarrow \text{EtOH} + \text{EtOCOO}^-,$$

$$\text{EtOCOO}^- \rightarrow \text{CO}_2 + \text{EtO}^-,$$

$$\text{EtO}^- + \text{ROH} \rightarrow \text{EtOR} + \text{OH}^-.$$

Scheme 2. Possible mechanism for ether formation.

The continuous decrease in activity for transesterification upon recycling can then be accounted for by, on one hand, the kinetic effect of the water contained in the reactants, and, on the other hand, by the development of the side reaction of hydrolysis of DEC and etherification of the alcoholic substrate.

4. Conclusions

In conclusion, a quantitative relation does exist between the catalytic activity and the basic properties of the catalysts employed for the transesterification reaction. MgLa mixed oxides and $CsF/\alpha\text{-}Al_2O_3$ were the best catalysts and could be recycled a few times. The high activity observed with $CsF/\alpha\text{-}Al_2O_3$ may be due to the higher nucleophilicity of the alcoholate formed as an intermediate, leading to a faster rate.

Acknowledgments

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