

Catalytic activity of rare-earth-supported catalysts in Friedel–Crafts acylations

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Abstract

Friedel–Crafts acylations are catalysed by rare-earth-supported catalysts. The preparation, characterization and performance of these solid catalysts in a test acylation reaction and in a variety of syntheses of aromatic ketones are reported. In contrast to the reactions using AlCl_3 , the experimental conditions are non-polluting and the final work-up does not require any aqueous treatment. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lewis acids, such as AlCl_3 , H_2SO_4 or BF_3 , etc., are well known for promoting Friedel–Crafts alkylation and acylation reactions [1–5]. However, because of the environmental problems due to the use of these homogeneous acid reagents, there has been a growing interest in using alternatives. Transition metal salts, especially chlorides and lanthanides—including scandium and yttrium—trifluoromethane sulfonates (triflates), have been frequently cited in literature. The first have been described as moderately active catalysts, because of their limited solubility [6], the second are described as soluble, reusable and active derivatives [7–11] but

the required quantities remain relatively high: 0.05 to 0.1 molar equivalent. In another way, environmentally friendly chemistry using solid and supported heterogeneous catalysts has been the subject of many reports in the past decade [12–22].

Smectite clays have been used as very effective supports for many transition metal salts, mainly zinc and copper chloride to give the catalysts named ‘Clayzic’ and ‘Claycuc’, respectively [23–32] [33–35], whereas rare-earth compounds, known to act as weak through strong Lewis acids, deposited on mineral supports have been seldom reported [36–39].

We have previously reported [40,41,46] that these supported lanthanides salts were very efficient catalysts of alkylation of aromatic compounds and we were consequently interested in demonstrating their catalytic activity in acylation reactions, K10 montmorillonite (an acidic

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and non-corrosive clay which belongs to the smectite class) and silica being used as the supports.

We report here catalytic Friedel–Crafts acylations using these catalysts and their preparation and characterization.

2. Results and discussion

2.1. Supported species characterization

Several kinds of supported lanthanides catalysts were prepared. We essentially studied two supports: the mesoporous acidic K10 montmorillonite clay [26,27,44] and column chromatography silicic oxide with a specific surface area of $230 \text{ m}^2 \text{ g}^{-1}$ and $500 \text{ m}^2 \text{ g}^{-1}$ respectively. A loading concentration of 1 mmol of rare-earth element per gram of support was used as a reference and by analogy with the concentration loading used for ‘Clayzic’ [23,24,26] in the benzylation of benzene with benzyl chloride. Three methods were used to prepare the catalysts: an aqueous way, written ‘a’ in the name of the catalyst, in which the hydrated salt was dissolved in water, a non-aqueous way, written ‘na’, in which the anhydrous salt was dissolved in THF, and a sol–gel way. In the sol–gel procedure, two methods of preparation were chosen, written ‘sg1’ and ‘sg2’. The last step of the catalysts preparation is called activation or calcination step in each method. The influence of the rare-earth chlorides: scandium, lanthanum, neodymium and ytterbium, as well as the influence of the thermal treatment on the catalytic activity, were examined.

Thermal activation by calcination at 280°C was chosen by analogy to the optimum calcination conditions determined for copper (II) chloride supported on K10 montmorillonite (‘Claycuc’) by Clark et al. [23] and Barlow et al. [24]. Thermal activations at 150°C and 550°C were also used, the first one corresponding to a drying step and the second one corresponding to a chemical transformation of the supported salt;

this point was suggested by the fact that evolution of hydrochloric acid gas occurred during the thermal treatments.

In an attempt to identify the nature of the supported species after the drying and calcination steps, we performed the following analyses.

The qualitative microanalysis (X probe) of the catalysts treated at 280°C showed the presence of the rare-earth and chlorine elements in the superficial layer (i.e., $1 \mu\text{m}$). The constituting elements of the support were also detected: O, Fe, Mg, Al, Si and K for K10 montmorillonite based catalysts.

By comparison of the experimental chlorine percentage found for catalysts **3** and **6**: 7.24% and 6.02%, respectively with the calculated percentage if the trichloride salt was the only species: 8.54%; it was established that the supported salt species was mainly trichloride (for K10- or silica-based catalysts). If rare-earth trichloride is the major form for the catalysts treated at 280°C , the minor form is likely to be the oxychloride. This hypothesis was confirmed by thermogravimetric analysis (ATG).

Fig. 1, relative to the hydrated salt $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, exhibits characteristic elimination of 6 molecules of water (33.4% weight loss) between 70°C and 180°C to give $\text{LaCl}_3 \cdot 1\text{H}_2\text{O}$. The weight loss observed between 325°C and 550°C corresponds to the transformation of $\text{LaCl}_3 \cdot 1\text{H}_2\text{O}$ into the oxychloride LaOCl .

A similar study was performed for the catalyst **6** treated at 280°C ; the thermogram is quite

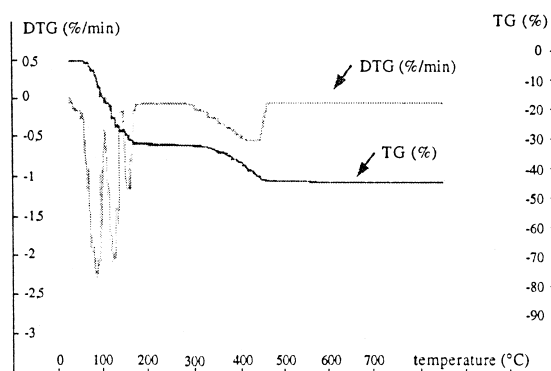


Fig. 1. TGA curve of the hydrated salt $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$.

different: the loss of weight is continuous and corresponds to the formation of oxychloride; an additional loss of weight was also observed after the formation of the oxychloride species. This phenomenon can be linked to the formation of the oxide species (La_2O_3).

The treatment at 550°C of the supported catalysts should thus lead to the formation of the oxide species. The influence of the support on the evolution of the supported salt under thermal treatment has been confirmed by the study of the catalyst **12** treated at 950°C .

XRD patterns of **12** compared to the patterns of the resulting product obtained from the unsupported salt $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ treated under the same conditions showed that the supported salt supported on silica is mainly transformed into the oxide species (La_2O_3) during the calcination step, whereas the unsupported salt gives the oxychloride species (LaOCl).

From these observations, we conclude that while trichloride is the predominant species at 280°C , a more complex mixture is formed for the catalysts activated at 550°C and over. Oxychloride and oxide are the most likely formed species but the presence of species linked to the support by O–Si bonds is also possible. Therefore, there is not only an influence of the thermal treatment on the nature of the supported salt but also an influence of the support. However, as the catalysts are used in acidic medium (HCl being eliminated as the reactions are proceeding), we can suggest that chloride species can be regenerated from the supported species. The thermogravimetric analysis of the catalyst **7** (removed after reaction from the mixture by filtration, then washed with toluene and finally dried under vacuum at 100°C) showed elimination of water and toluene at 60°C . Other eliminations below $300\text{--}350^\circ\text{C}$, corresponding to adsorbed compounds, were also determined. Weight losses observed between 350°C and 700°C were probably due to chlorine elimination as the area corresponds to LaOCl formation from lanthanum trichloride (or $-\text{O}-\text{La}-\text{Cl}_2$ type species) regenerated during the reaction.

Moreover, it has been reported [45] that the calcination process causes structural modifications in the mesoporous K10 montmorillonite and that this process is more complex than a simple dehydration. It has been mentioned that calcination of K10 montmorillonite may cause the destruction of some of the mesopores and that there is consequently little residual lamellar structure in the catalysts (both doped and undoped support) [26].

2.2. Performance of the solid catalysts in the benzoylation of anisole with benzoyl chloride

The effects of the different thermal treatments on the activity of the catalysts have been determined using benzoylation of anisole with benzoyl chloride as a test reaction. This convenient reaction gives 4-methoxybenzophenone as the predominant product. The effects of the nature of the rare earth deposited on the support and of the support itself were examined in the same reaction.

The comparison of the conversion rate of anisole (Fig. 2) leads to the conclusion that optimum activity (the highest rate of anisole conversion) was obtained using a catalyst heated

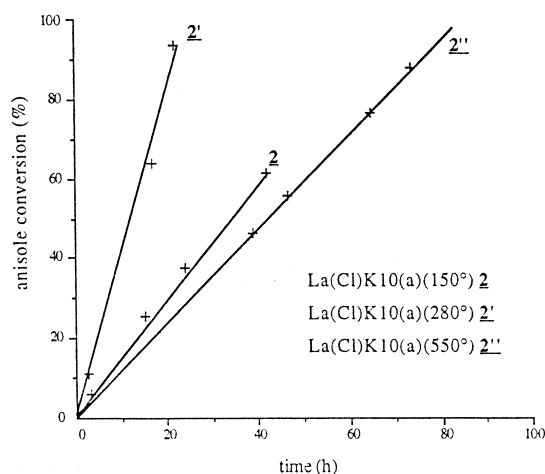


Fig. 2. Influence of the thermal treatment on the catalytic activity of the K10 supported catalysts in the acylation of anisole with benzoyl chloride.

at 280°C (**2'**) for a salt loading of 1 mmol/g of support. At 154°C, reaction of anisole with benzoyl chloride with **2'** as the catalyst gave 50% of conversion of anisole in 15 h and 95% in 24 h. **2** gives similar performance as **2'**. The *para/ortho* isomer ratio was 95/5 in all reactions. If residual water can explain the lower activity of the catalyst **2** treated at 150°C, compared to **2'**, changes of the clay structure or of the nature of the supported salt during the calcination process could explain the lower activity of **2''** treated at 550°C. These facts are in good accordance with the results described in literature [23,24].

With silica-based catalysts, prepared from trichloride salts, data clearly indicate (Fig. 3) that the temperature does not affect so strongly the performances of the catalysts: **6** is the most efficient catalyst, but **7** and **8** exhibit quite similar activity. Then it appears that the loss of activity recorded for the K10 based catalysts can be attributed to a modification of the support which does not occur in the case of the silica based catalysts. When the catalyst is prepared from an acetate salt, the best results are obtained after a calcination at 550°C. In this range of temperature, the nature of the deposited substance is obviously altered, an oxide may be formed.

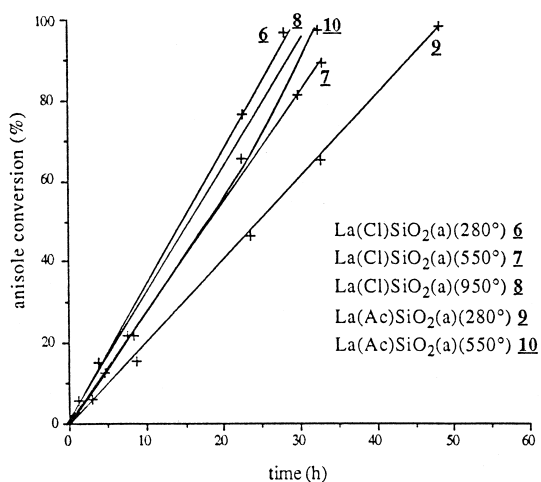


Fig. 3. Influence of the anion of the rare-earth salt used and of the thermal treatment on the catalytic performances.

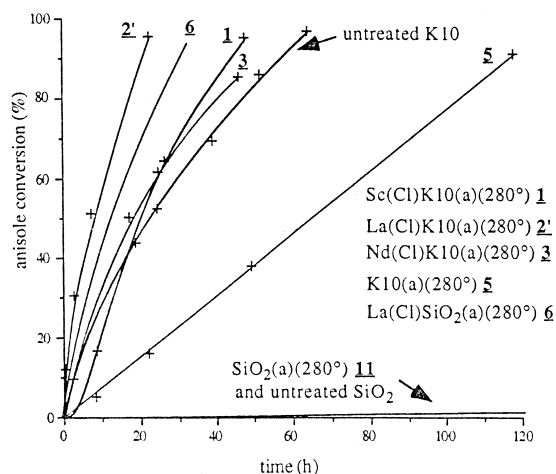


Fig. 4. Influence of the rare earth deposited on a support on the rate of the acylation of anisole with benzoyl chloride.

In Fig. 4, the percentages of anisole conversion in the benzylation of anisole are plotted as a function of time for reactions with lanthanum, neodymium and scandium salt deposited on K10 as well as with both treated and untreated K10. It can be seen that the rare-earth-supported catalysts are all active in the benzylation of anisole: the catalyst **2'** ((La)(Cl)K10(a)(280°)) leads to a slightly higher rate of anisole conversion than **1** and **3** but the difference can't be easily linked with their respective Lewis acidity. The performances of **4** are quite identical to that of **1** and **3** but are not reported in the figure for clarity. By comparing the performances of **2''** and **6** (respectively (La)(Cl)K10(a)(280°) and (La)(Cl)-SiO₂(a)(280°)) with their respective supports **5** (K10(a)(280°)) and **11** (SiO₂(a)(280°)), treated under the same conditions, we can evaluate the participation of the rare-earth salt to the catalytic activity. The figure shows that, in contrast to the clay, which contains Brönsted acid sites, silica (either treated or untreated) does not participate to the catalytic process. Silica is consequently a good support to estimate the own activity of the rare-earth salt. We can also see that the untreated K10 montmorillonite clay catalyses the benzylation of anisole with a higher conversion rate than the treated support (**5**). This can be explained by the fact that the

aqueous and thermal treatments, generally considered as more complex than a simple dehydration as said before, modify the structural features of the K10 montmorillonite, mainly its porosity and its lamellar structures [26]. From these results, we can point out the greater activity of the rare-earth-supported catalysts over the undoped supports, the best results being obtained with catalysts containing both Brönsted and Lewis acid sites (**1**, **2''** and **3**).

The non-aqueous method avoids use of water, solvent which requires a relatively long drying step, but implies the preparation of a non organic soluble lanthanide salt, generally a THF adduct of the anhydrous trichloride. Fig. 5 shows a comparison of supported catalysts prepared via non-aqueous and aqueous methods. This study was done in an identical way as for the reactions described in Fig. 2. The best activity is recorded for the treatment at 280°C (**14**), activity which is higher than that of **3**.

The results of the catalytic tests performed with the third class of catalysts, obtained via sol–gel preparation, are shown in Fig. 6. Only one activation temperature (550°C) was tested; this choice corresponds to the required treatment for acetate species destruction. The catalysts so obtained are less efficient than the more conventional **7**; **16** shows a poor activity, when **17** and **18** prepared by the same method (sg2) do not behave similarly as expected. Then it appears that the sol–gel preparations which are

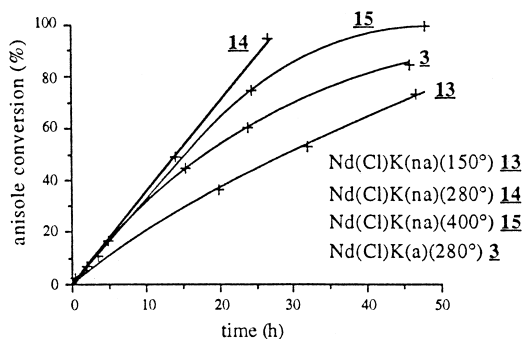


Fig. 5. Comparison of supported catalysts prepared by the non-aqueous method and influence of the thermal treatment on the catalytic activity.

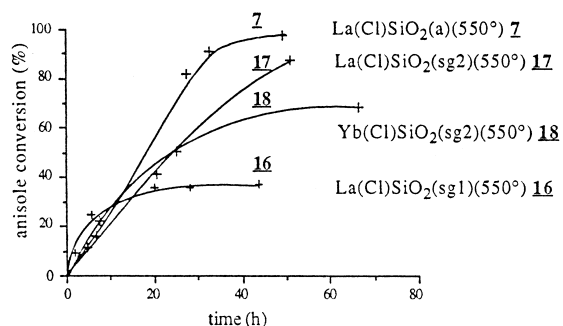


Fig. 6. Comparison of the performances in the benzylation of anisole of catalysts prepared via sol–gel methods and aqueous method.

more complexes could also lead to non reproducible performances. These investigations were thus not developed.

It has been shown that these catalysts are reusable in Friedel–Crafts alkylations, with a weak loss of activity. This loss of activity was related to a partial redissolution of the lanthanide chloride in the organic reagents. Then, a part of the global catalytic activity might be due to a homogeneous catalysis from lanthanide trichloride in solution. To estimate the part of the homogeneous catalysis, the same experiment has been performed with anhydrous lanthanum trichloride in the rate 1/5000. After 24 h refluxing, only 5% of the expected acylated compound was present.

2.3. Catalytic activity of the supported catalysts in a variety of acylation reactions

Among the catalysts screened, **3** was found to be one of the most effective. On the basis of the results described above, we can say that K10 montmorillonite based rare-earth catalysts activity is due to both Lewis and Brönsted acid sites.

We now report a series of reactions catalysed by this catalyst to demonstrate its general applicability to Friedel–Crafts reactions. The catalyst **6** was also tested and the performances are described in this section. The molar ratio of aromatic substrate/acetyl halide/catalyst and the results (distribution of the products and isomers

distribution) of the reactions are summarized in Table 1. The reactions were carried out with vigorous stirring and followed by periodical sampling.

Data of Table 1 prove the dependence of both the substrates and the acylating reagents on the reaction rate. Although the acylation of benzene with benzoyl chloride did not occur (entry 1), thiophene (entry 2) and naphthalene (entry 3) were C-acylated with a good conversion rate (110 and 150 cycles h^{-1} , respectively) with **3** as the catalyst. The reaction rate was increased by using reagents containing electron donating groups: anisole (entry 4) and 2-methoxynaphthalene (entry 5) were C-acylated to give 4-methoxybenzophenone and 2'-methoxy-1'-ben-

zonaphthone, respectively as the predominant products, with a reaction rate of 330 and 2000 cycles h^{-1} (Fig. 7). The observed relative rates are also influenced by the activation of the acylating reagents. Whereas the rate of the 2-methoxynaphthalene acylation with tertio-butyl chloride was low (6 cycles h^{-1} ; entry 6) for both steric hindrance and temperature reasons. The rate was increased in the case of acylation reactions with octanoyl chloride (entry 7) and cyclohexanecarboxylic acid chloride (entry 8): 630 cycles h^{-1} and 2000 cycles h^{-1} were obtained respectively with **3** (see also Fig. 8). Benzoic anhydride was found less effective than benzoyl chloride in the acylation of anisole (entries 9 and 10) with **6** as the catalyst, benzoyl

Table 1
Friedel–Crafts acylation reactions catalysed by solid acid catalysts

Entry	Catalyst (mg)	Acylating reagent (mmol)	Substrate	Reagent/Ln molar ratio	T (°C)	Turnover (cycles h^{-1})	Isomer distribution
1	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	Benzene	5000 (b)	75	–	–
2	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	Thiophene	5000 (b)	84	110	98% α , 2% β
3	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	Naphthalene	5000 (b)	160	150	48% α , 52% β
4	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	Anisole	5000 (b)	154	330	4% o, 96% p
5	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	2-Methoxynaphthalene	5000 (b)	160	2000	89% (2'-1'), 5% (3'-2'), 6% (6'-2')
6	(Nd)(Cl)K10(a)(280°) 3	tBuCOCl	2-Methoxynaphthalene	100 (b)	105	6	89% (2'-1'), 3% (3'-2'), 8% (6'-2')
7	(Nd)(Cl)K10(a)(280°) 3	C ₈ H ₁₅ COCl	2-Methoxynaphthalene	1000 (b)	194	630	84% (2'-1'), 3% (3'-2'), 13% (6'-2')
8	(Nd)(Cl)K10(a)(280°) 3	RCOCl (c)	2-Methoxynaphthalene	5000 (b)	184	2000	42% (2'-1'), 25% (3'-2'), 8% (7'-1'), 25% (6'-2')
9	(La)(Cl)SiO ₂ (a)(280°) 6	PhCOCl	Anisole	5000 (a)	154	175	4% o, 96% p
10	(La)(Cl)SiO ₂ (a)(280°) 6	(PhCO) ₂ O	Anisole	5000 (a)	"	65	5% o, 95% p
11	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	2-Methoxynaphthalene	100 (b)	198 (d)	≥ 96	93% (2'-1'), 3% (3'-2'), 4% (6'-2')
12	(Nd)(Cl)K10(a)(280°) 3	PhCOCl	2-Methoxynaphthalene	100 (b)	65 (e)	12	91% (2'-1'), 4% (3'-2'), 5% (6'-2')

(a) Substrate/Ln = 5000.

(b) Acylating reagent/Ln = 5000.

(c) RCOCl: cyclohexanecarbonyl chloride.

(d) Under reflux of PhCOCl.

(e) Under reflux of hexane used as the solvent.

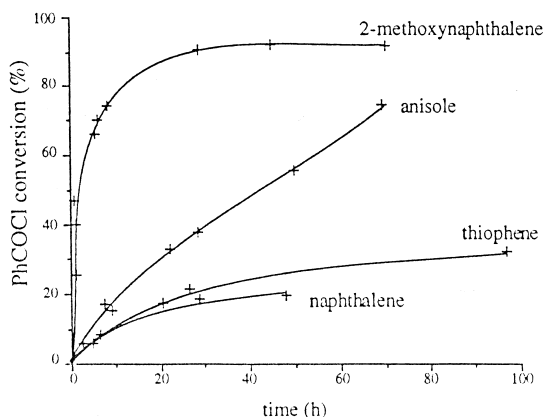


Fig. 7. Influence of the substrate activation on the rate of acylation reactions with benzoyl chloride.

chloride giving higher reaction rate (for a similar regioselectivity) (see also Fig. 9). Entries 11 and 12 point out the influence of the reaction temperature and effect of the solvent on the reaction rate: the turnover was reduced from 96 to 12 cycles h^{-1} in presence of hexane (whose low boiling point limits the temperature).

Although alkylation reactions have been usually shown as poorly selective (because of polyalkylation reactions and rearrangements) [29], regioselectivity was generally obtained in the acylation reactions.

In conclusion, we have established that thermally activated rare-earth salts deposited on solid inorganic supports are very efficient catalysts of acylation of aromatic substrates. We

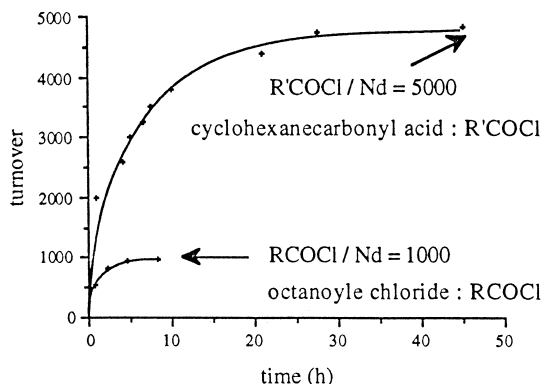


Fig. 8. Influence of the acylating reagent activation on the rate of the 2-methoxynaphthalene acylation.

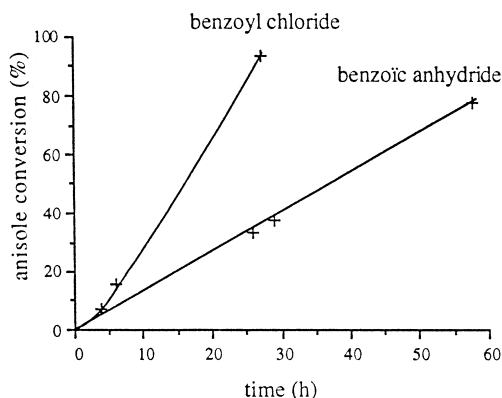


Fig. 9. Comparison of the reactivity of benzoyl chloride and benzoic anhydride towards anisole.

have also shown that the nature of the active species is a function of the temperature of calcination. The remarkable activity of these rare-earth supported reagents is consequently in contrast to the unsupported salts described in literature.

Among the supports used, acidic K10 montmorillonite clay is shown to give the more effective catalysts as the clay has its own activity.

The major advantages of the solid acid catalysts here described are their good activity, as well as their easy removal from the reaction mixture.

Moreover, the catalysts are environmentally friendly catalysts as they prevent hazardous waste for the environment.

3. Experimental

3.1. Materials

Commercially available organic and inorganic solvents and reagents were used without further distillation or purification except for THF that was distilled before use. The pure hydrated lanthanide salts were purchased by Rhône-Poulenc. The anhydrous chlorides were prepared following the described procedures [42]. K10 montmorillonite and column chromatography

silica were provided from Aldrich and used without further treatment.

The thermal treatments were performed in a tubular oven (21100 Thermolyne), in air for heating and under nitrogen atmosphere for cooling steps.

3.2. Analytical techniques

Composition and yields of the reaction products were determined with a GC8000 Series gas chromatograph equipped with a flame ionization detector, a Data Jet Integrator (Thermo Separation Products) and a 25 m × 0.32 mm OV1 capillary column or a 30 m × 0.53 mm OV624 semi-capillary column.

¹H and ¹³C NMR spectra were recorded on a Bruker AC200 (200 MHz) in CDCl₃ as internal reference ($\delta = 7.25$ ppm).

Mass spectra were obtained on a GC/MS coupled spectrometer (Hewlett Packard G1800A GCD) equipped with a flame ionization detector and a 30 m × 0.25 mm HP5 capillary column.

Elemental (C, H) analyses were carried on a EA 1108 CHNS-O (Fisons Instruments).

Thermogravimetric analyses (TGA) were carried on a Setaram TGA92, under nitrogen atmosphere. The heating rate was 5°C/min. The samples were placed in platinum crucibles.

X-ray diffraction (XRD) studies were performed on a diffractometer INEL CPS 120 (Cu-K α_1 monochromatized radiation).

Differential Scanning Calorimetry (DSC) curves were run on a Mettler DSC 12E instrument. The samples were placed in platinum crucibles and the results obtained with the Mettler TA89E program.

3.3. Preparation of the supported catalysts

3.3.1. Aqueous preparation

The catalysts **1–4** and **6–10** were prepared by dissolving 5 mmol of the rare-earth salt (1.8 g of NdCl₃·6H₂O for **3**) in 100 ml of water at room temperature, under vigorous stirring, then

by adding 5 g of the support in the solution, for a resulting loading of 1 mmol g⁻¹. After 6 to 8 h of stirring at room temperature, water was removed under reduced pressure. The solid was then dried 4 h at 100°C and thermally activated 5 h at 150°C then 7 h at 280°C (for **3**).

The general thermal treatments were as follows for the other supported catalysts: 5 to 6 h at 150°C, 7 to 8 h at 280°C, 3 h at 550°C in a consecutive way. The temperature indicated in the name of the catalyst corresponds to the highest temperature of the activation program.

Blank samples: K10(a)(280°) **5** and SiO₂(a)(280°) **11** were prepared using a similar method, without adding any rare-earth salt.

Prepared catalysts (from the corresponding hydrated metallic salt): (Sc)(Cl)K10(a)(280°) **1**; (La)(Cl)K10(a)(150°) **2**; (La)(Cl)K10(a)(280°) **2'**; (La)(Cl)K10(a)(550°) **2''**; (Nd)(Cl)K10(a)(280°) **3**; (Yb)(Cl)K10(a)(280°) **4**; (La)(Cl)SiO₂(a)(280°) **6**; (La)(Cl)SiO₂(a)(550°) **7**; (La)(Cl)SiO₂(a)(950°) **8**; (La)(Ac)SiO₂(a)(280°) **9**; (La)(Ac)SiO₂(a)(550°) **10**.

The catalyst (La)(Cl)(SiO₂)(a)(950°) **12** was prepared as follows: 10 mmol of LaCl₃·7H₂O (3.71 g) were dissolved in 100 ml of water, 10 g of silica were added and the mixture was vigorously stirred for 6 h. Elimination of the solvent under reduced pressure was followed by a drying step of 16 h at 100°C in air and by an activation step of 1 h at 950°C.

3.3.2. Non-aqueous preparation

The catalysts **13**, **14** and **15** were prepared under nitrogen atmosphere. A typical procedure is described for **13**. The adduct NdCl₃(THF)₃ was first obtained in 90% yield by soxhlet extractions of anhydrous NdCl₃ in THF, concentration of the solution and crystallisation [43]. In a second step, 2 g of K10 montmorillonite (dried at 150°C), 2 mmol of NdCl₃(THF)₃ (0.467 g) and 20 ml of THF were mixed at room temperature and vigorously stirred during 16 h. THF was then removed under reduced pressure and the solid was dried at 150°C (4 h) to give

13, **14** was obtained from **13** by extending the thermal treatment (30 min at 280°C), **15** from **14** by extending the thermal treatment (7 h 30 at 400°C). Prepared catalysts: (Nd)(Cl)K10(na) (150°) **13**; (Nd)(Cl)K10(na)(280°) **14**; (Nd)(Cl)-K10(na)(400°) **15**.

3.3.3. 'Sol-gel' preparation

The 'sol' was obtained by dissolving 2 mmol of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.74 g) in 2 ml of water, then by adding this solution to an aqueous solution of ammonium acetate (2.7 mol l^{-1}). Fifteen milliliter of water and 2 g of silica were added in the previous mixture. To this mixture, stirred at room temperature during 1 h 30, were finally added 2 ml of an ammonia solution (1 mol l^{-1}). Water was removed under reduced pressure after homogenization and impregnation of the support at room temperature during 20 min to give finally **16** after thermal treatment at 550°C (method sg1). **17** was obtained in an identical way, except the fact that the ammonia solution was added before adding silica in the mixture (method sg2). Prepared catalysts: (La)(Cl)- $\text{SiO}_2(\text{sg}1)(550^\circ)$ **16**; (La)(Cl) $\text{SiO}_2(\text{sg}2)(550^\circ)$ **17**; (Yb)(Cl) $\text{SiO}_2(\text{sg}2)(550^\circ)$ **18**.

3.4. Acylation reactions: typical experiment

Benzoyl chloride (12.08 g, 86 mmol), anisole (5.4 g, 50 mmol) and 10 mg of the solid catalyst (in ca. 1/5000 mol equiv in relation to anisole) were refluxed (154°C) in air under vigorous stirring. The reaction course was followed by periodical samplings (GC). After consumption of anisole, the solution was cooled and the catalyst was separated by filtration. Fifty milliliters of diethyl ether then 100 ml of an aqueous solution of sodium hydroxide (NaOH, 2 N) were added in the reaction mixture. After stirring overnight, drying of the ether phase, filtration and removing of the solvents, 4-methoxybenzophenone was obtained (9.12 g, 86% yield).

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References

- [1] G.A. Olah, Friedel-Crafts and Related Reaction, Interscience Ed., Vol. III, Part 1, New York, 1964.
- [2] J.N. Kim, K.H. Chung, E.K. Ryu, *Tetrahedron Lett.* 35 (1994) 903.
- [3] K.H. Chung, J.N. Kim, E.K. Ryu, *Tetrahedron Lett.* 35 (1994) 2913.
- [4] S.H. Baek, *J. Chem. Res. (S)* (1994) 451.
- [5] S. Pivsa-Art, K. Okuro, M. Miura, S. Murata, M. Nomura, *J. Chem. Soc., Perkin Trans. 1* (1994) 1703.
- [6] N. Mine, Y. Fujiwara, H. Taniguchi, *Chem. Lett.* (1986) 357.
- [7] K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, *J. Am. Chem. Soc.* 117 (1995) 4413.
- [8] K. Ishihara, M. Kubota, H. Yamamoto, *Synlett* (1996) 265.
- [9] A. Kawada, S. Mitamura, S. Kobayashi, *Chem. Commun.* (1996) 183.
- [10] T. Tsuchimoto, K. Tobita, T. Hiyama, S.I. Fukuzawa, *Synlett* (1996) 557.
- [11] S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* 120 (1998) 2985.
- [12] V.G. Kumar, T.S. Shoba, K. Rao, *Tetrahedron Lett.* 26 (1985) 3281.
- [13] K.R. Sabu, R. Sukumar, M. Lalithambika, *Bull. Chem. Soc. Jpn.* 66 (1993) 3535.
- [14] O. Aleksziuk, S.E. Biali, *Tetrahedron Lett.* 34 (1993) 4857.
- [15] J.H. Clark, D.J. Macquarrie, *Chem. Soc. Rev.* 25 (1996) 303.
- [16] G. Gondos, I. Kapocsi, *J. Phys. Chem. Solids* 57 (1996) 855.
- [17] S. Narayanan, K. Deshpande, *Appl. Catal. A* 135 (1996) 125.
- [18] R. Ashforth, J.R. Desmurs, *The Roots of Organic Development*, Elsevier, Industrial Chemistry Library 8, 1996, 3.
- [19] A.K. Pandey, A.P. Singh, *Catal. Lett.* 44 (1997) 129.
- [20] J.H. Clark, A.J. Butterworth, S.J. Tavener, A.J. Teasdale, S.J. Barlow, T.W. Bastock, K. Martin, *J. Chem. Technol. Biotechnol.* 68 (1997) 367.
- [21] A.Y. Jogalekar, R.G. Jaiswal, R.V. Jayaram, *J. Chem. Technol. Biotechnol.* 71 (1998) 234.
- [22] V. Quaschnig, J. Deutsch, P. Druska, H.-J. Niclas, E. Kemnitz, *J. Catal.* 177 (1998) 164.
- [23] J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow, P. Landon, *J. Chem. Soc., Chem. Commun.* (1989) 1353.

- [24] S.J. Barlow, J.H. Clark, M.R. Darby, A.P. Kybett, P. Landon, K. Martin, *J. Chem. Res. (S)* (1991) 74.
- [25] S.J. Barlow, T.W. Bastock, J.H. Clark, S.R. Cullen, *Tetrahedron Lett.* 34 (1993) 3339.
- [26] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastock, *J. Chem. Soc., Perkin Trans. 2* (1994) 1117.
- [27] C.N. Rhodes, M. Franks, G.M.B. Parkes, D.R. Brown, *J. Chem. Soc., Chem. Commun.* (1991) 804.
- [28] C.N. Rhodes, D.R. Brown, *J. Chem. Soc., Faraday Trans. 89* (1993) 1387.
- [29] D.R. Brown, C.N. Rhodes, *Catal. Lett.* 45 (1997) 35.
- [30] P. Laszlo, A. Mathy, *Helv. Chim. Acta* 70 (1987) 577.
- [31] A. Cornéilis, P. Laszlo, S. Wang, *Tetrahedron Lett.* 34 (1993) 3849.
- [32] A. Cornéilis, C. Dony, P. Laszlo, K.M. Nsunda, *Tetrahedron Lett.* 32 (1991) 2903.
- [33] O. Sieskind, P. Albrecht, *Tetrahedron Lett.* 34 (1993) 1197.
- [34] A. Cornéilis, P. Laszlo, S.F. Wang, *Catal. Lett.* 17 (1993) 63.
- [35] B.P. Choudari, S. Mutyala, M.L. Kantam, K.V. Prasad, *Appl. Catal. A* 171 (1998) 155.
- [36] B.H. Chiche, A. Finiels, C. Gauthier, P. Geneste, *J. Mol. Catal.* 42 (1987) 229.
- [37] T. Imai, A. Kocal, *US Pat.* (1989) 5,003,121.
- [38] P.R. Kurech, J.S. Holmgren, *US Pat.* (1991) 5,214,211.
- [39] K. Gaare, D. Akporiaye, *J. Mol. Catal. A, Chem.* 109 (1996) 177.
- [40] D. Baudry, A. Dormond, F. Montagne, J.R. Desmurs, *FR Pat.* (1996) 96024.
- [41] D. Baudry, A. Dormond, F. Montagne, *C.R. Acad. Sci.-Série IIc* (1998) 41.
- [42] M.D. Taylor, C.P. Carter, *J. Inorg. Nucl. Chem.* 24 (1962) 387.
- [43] M. Visseaux, A. Dormond, D. Baudry, *Bull. Chem. Soc. Chim. Fr.* 130 (1993) 173.
- [44] C.N. Rhodes, D.R. Brown, *J. Chem. Soc., Faraday Trans.* 88 (1992) 2269.
- [45] M. Devic, J.P. Shirman, A. Decarreau, G. Bram, A. Loupy, *New J. Chem.* 15 (1991) 949.
- [46] D. Baudry, A. Dormond, F. Montagne, *New J. Chem.* 18 (1994) 871.