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Transesterification of acrylates by heterogeneous basic catalysis

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ABSTRACT

Different solid basic catalysts including CsF/αAl_2O_3, KF/αAl_2O_3, $Ca(NO_3)_2/\gamma Al_2O_3$, $NaNO_3/\gamma Al_2O_3$, $LiNO_3/\gamma Al_2O_3$ were evaluated for the transesterification of ethyl acrylate by n-hexanol. All of them are active and selective in the transesterification reaction under mild conditions and without solvent, using a 1/1 molar ratio of reactants. Ca/γAl_2O_3 was shown to be the most selective of this set of catalysts and it could be recycled three times without lost of selectivity.

1. Introduction

The development of industrial processes with low environmental impact has become one of the main issues of sustainable chemistry. The replacement of liquid acids and bases by solid catalysts in organic reactions is interesting since it would combine the advantages of processes less harmful for environment, with those of easier separation from the reaction mixture, and the possibility of recycling. However, this replacement is still a challenge particularly in the field of catalysis by solid bases. Solid bases have found an important number of useful applications in chemical industry. They have been proposed as heterogeneous catalysts for several processes such as olefin isomerization, aldol condensation, production of fatty acid methyl esters from natural fats, Guerbet condensation, epoxide ring-opening, NOx adsorption and reaction [1]. Acrylates are mainly used in polymerization reactions and those polymers have a large number of industrial applications. The transesterification reaction provides the appropriate way for obtaining some acrylates hardly prepared by esterification reactions catalyzed with acid catalysts [2]. At the industrial scale, transesterification is carried out using homogeneous catalysts, alkyl titanates are preferred involving considerable problems with separation and heterogeneous catalysis would then be attractive.

Methyl and ethyl esters were initially produced by the treatment of ethylene cyanohydrin with the appropriate alcohol in the presence of sulfuric acid, but this method was less suitable for the production of higher alkyl acrylates. The first publication on the synthesis of n-alkyl acrylates was reported by Rehberg and Fischer [3], using methyl acrylate and the corresponding alcohol using sulfuric acid or p-toluene sulfonic acid as catalyst, and hydroquinone or p-phenylenediamine as polymerization inhibitors. The reaction mixture composed of methyl acrylate, alcohol (molar ratio acrylate/alcohol = 3), hydroquinone and catalyst was heated in a glass flask attached to a fractionating column, the system was left at reflux until the formation of the azeotrope began, which was removed as it was formed. When formation of azeotrope ceased, the mixture was fractionally distilled and the ester formed was recovered. The authors reported high yields to acrylic esters having two to sixteen carbon atoms in the alkyl group. Sulfuric acid was preferred as catalyst and was used in the concentration of 0.5 mol acid per mol of alcohol with 3–5% by weight hydroquinone based on acrylate [3].

In another publication Rehberg et al. [4] studied the influence of the structure of the alcohol in the alcoholysis reaction of methyl acrylate, using the method described in his previous work [3]. They reported good yields and higher reaction rates for the preparation of alkyl acrylates from secondary alcohols. Very few attempts have been reported concerning heterogeneous catalysis used in the transesterification of acrylates; up to now they have been limited to approaches based on surface organometallic chemistry: silica-supported zirconium compounds have been reported by Salinier et al. [5,6] and polymer anchored Ti compounds by Alves et al. [7]. However, the active species are systematically leached during the reaction due to the metal alkoxide hydrolysis and alcoholysis [8].

Transesterification occurs by an acid–base mechanism, and usual solid bases could be active and more easily recycled than the heterogeneized metal alkoxide analogues. The aim of this study was

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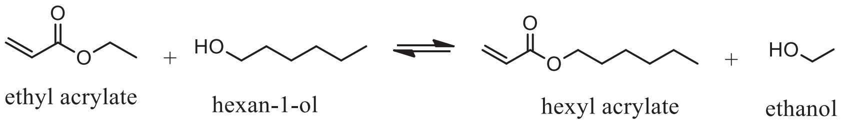


Scheme 1. Transesterification reaction of ethyl acrylate with n-hexanol.

to evaluate the catalytic behaviour of solid bases in the transesterification reaction of acrylates. We investigated the transesterification of ethyl acrylate with n-hexanol to synthesize hexyl acrylate as a model reaction (Scheme 1).

In this exploratory study a series of solid bases has been compared. From previous works [9–11] it appears that CsF or KF shows a higher basicity when supported on α-Al_2O_3 than on γ-Al_2O_3. This has been attributed to the reaction of the fluoride with the support: γ-Al_2O_3 has an acidic character and reacts easily with the basic fluoride, whereas α-Al_2O_3 has a much lower reactivity and permits to retain part of the fluoride as CsF or KF. Alkalines supported on γ-Al_2O_3 have also been shown to be strong bases [12]. The basic strength is usually related to the size of the cations, and the comparison of a series of cations of increasing size can give a representation of the effect of the basic strength on the catalytic properties.

2. Experimental

2.1. Preparation of catalysts

2.1.1. CsF/α-Al_2O_3, KF/α-Al_2O_3

The support used was α-alumina (SPH 512, 10.5 m^2/g, Rhône-Poulenc). We used the method of incipient impregnation, using 1 mmol of KF or CsF for 1 g of alumina [13]. Water was evaporated a 323 K then the solid was dried at 373 K. The catalysts were pretreated before reaction for 4 h, under air flow at 373 K. According to previous work [13] these conditions favour the crystallization of the fluoride avoiding the reaction with the support which is observed at high temperature.

2.1.2. $Ca(NO_3)_2$, $NaNO_3$, $LiNO_3$ supported on γ-Al_2O_3

These samples were prepared by grinding the γ-alumina (SCP-350, 400 m^2/g, Rhône-Poulenc), with the precursor salt ($Ca(NO_3)_2$, $NaNO_3$, $LiNO_3$), as first reported by Zhu et al. [12]. The ratio metal/alumina was fixed to 5 mmol/g per g of alumina. The mixture was first ground in a mortar down to 200 mesh, then water (0.5 mL g^{-1} of alumina) was added. The paste was then mixed for 10 min and dried at 383 K for 12 h. The catalysts were pre-treated before reaction for 2 h in an air flow at 723 K.

2.2. Catalysts characterization

Elemental chemical analyses were obtained by chemical plasma optical emission (ICP-OES), using “Activa” equipment from **Jobin Yvon**, and the catalysts samples dissolved with $HClO_4 + HNO_3 + HF$. Specific surface areas were determined by nitrogen adsorption at 77 K using a **Micromeritics ASAP 2020** equipment. Samples were previously degassed *in situ* at 623 K under vacuum for 3 h. Surface areas were calculated using the Brunauer–Emmet–Teller (BET) methods over a P/P_0 range where a linear relationship was obtained. X-ray diffraction (XRD) powder patterns were collected on a **Bruker D5005** diffractometer equipped with an Cu anode, using Kα1 + α2 (λ = 1.54184 Å) as radiation source. Data were recorded over a 2θ range of 4–80° with an angular step of 0.02° at 1 s/step. Basicities were characterized by microcalorimetry using CO_2 adsorption at 303 K with a **Tian-Calvet calorimeter** on samples activated in vacuum at 723 K for 3 h. Acidities were characterized by temperature programmed desorption of ammoniac (TPD-NH_3); analysis were performed with 200 mg of the catalyst; first the temperature was increased to 450 °C, and kept for 30 min to desorb CO_2 and H_2O adsorbed on the catalyst surface. Subsequently, the catalyst was cooled to 25 °C and contacted with a gaseous flow 50 mL min^{-1} NH_3/He 0.3% in 30 min, to allow saturation. The weakly adsorbed ammonia was allowed to desorb by passing a flow of He for 30 min. Finally the temperature was raised to 400 °C. NH_3-TPD analyses were carried out in a device **Belcat-M**, BEL JAPAN INC equipped with a TCD detector.

2.3. Catalytic reaction of transesterification of ethyl acrylate with n-hexanol

The reaction was carried out in a 100 mL flask equipped with a condenser and magnetic stirrer. The required amount of alcohol, solvent, and the freshly activated catalyst (0.5 g), were introduced under N_2 atmosphere in the reactor placed in the oil bath. The temperature was raised up to the reaction temperature (353, 373, and 403 K). After reaching the reaction temperature, the required amount of ethyl acrylate was added, and the reaction started. The influence of the molar ratio R of alcohol/acrylate was evaluated in the range 2–6. The analyses of the reaction mixture were made by gas chromatography using a Supelcowax (polar polyethylene glycol) capillary column (30 m × 0.25 mm, 0.25 μm). The chromatograph was calibrated for the different reactants and products. The material balance was better than 95%. The conversion was calculated from the decrease of the peak of ethylacrylate, the molar yield from the molar ratio hexylacrylate formed to ethylacrylate consumed, and the selectivity from the ratio yield/conversion.

The non catalyzed process was investigated using DMF as solvent at 373 K: the conversion was below 1% and it can then be concluded that the reaction does not proceed in the absence of a catalyst.

3. Results and discussion

3.1. Catalysts characterization

The XDR pattern of CsF/α-Al_2O_3 catalyst shows the presence of phases as α-Al_2O_3, $CsAlF_4$, $CsHCO_3$, Cs_3AlF_6 in agreement with previous reports [9,10], but also CsF, which was detected only after the heat treatments beyond 423 K. Ni et al. [10] reported that Cs is present as Cs_2O, CsOH or Cs_2CO_3, highly dispersed and not detected by XDR. It was observed that the alumina support retained its structure (Figs. 1 and 2) that allows us to say that the reaction with fluoride is limited to the surface. The XDR pattern of KF/α-Al_2O_3 (Figs. 3 and 4) revealed the presence of K_3AlF_6, $KHCO_3$ and α-Al_2O_3, without the presence of KF phase, which has been reported previously on this type of catalyst at higher KF content [11,13]. Again, we can say that the KF dispersion did not modify the XRD structure of the alumina support, the interaction with KF being limited to the surface.

Loading γ-Al_2O_3 with Na, Li, Ca leads to distinct modifications of the alumina support: upon Ca loading, the alumina support remains mainly amorphous and the formation of Ca aluminates is only detected on the XRD pattern, together with the original peak of the γ-Al_2O_3 (Fig. 5). By contrast the systems $LiNO_3$/γ-Al_2O_3

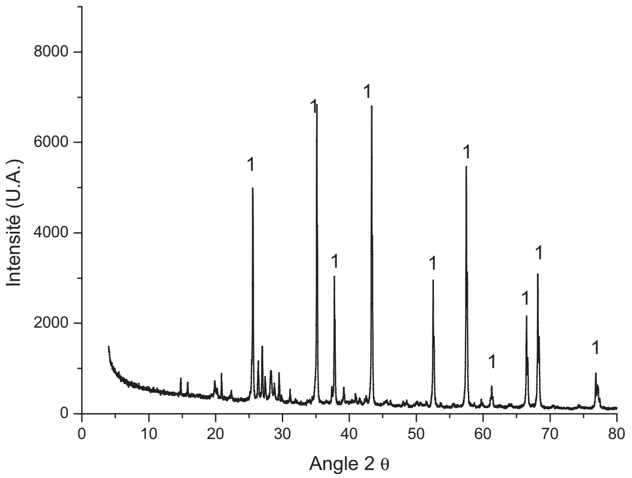


Fig. 1. XDR pattern of CsF/α-Al_2O_3 pre-treated 4 h at 373 K under air flow; (1) α-Al_2O_3 (corindon).

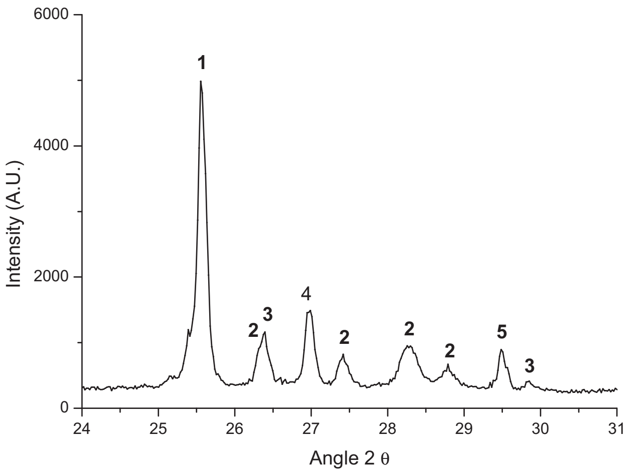


Fig. 2. XDR pattern CsF/α-Al_2O_3 pre-treated 4 h at 373 K under air flow between 24 and 31 2θ angles: (1) α-Al_2O_3, (2) $CsAlF_4$, (3) $CsHCO_3$, (4) Cs_3AlF_6 and (5) CsF.

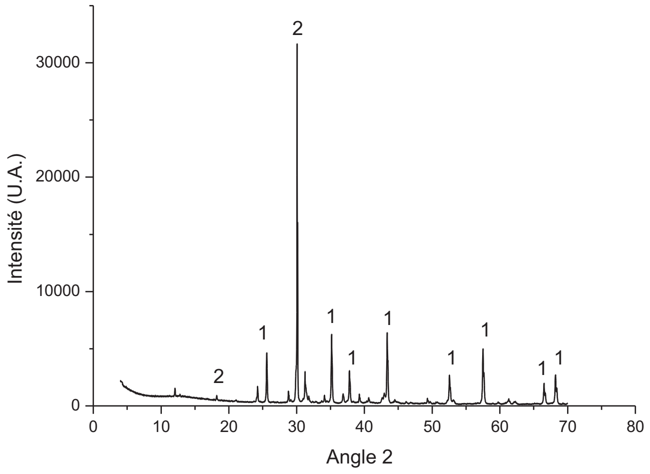


Fig. 3. XDR pattern of KF/α-Al_2O_3 pre-treated 4 h at 373 K under air flow: (1) α-Al_2O_3 (corindon) and (2) K_3AlF_6.

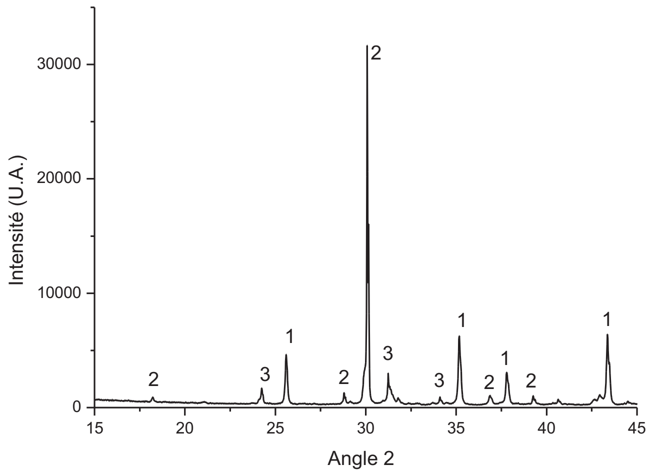


Fig. 4. XDR pattern of KF/α-Al_2O_3 pre-treated 4 h at 373 K under air flow between 15 and 45 2θ angles: (1) α-Al_2O_3 (corindon), (2) K_3AlF_6 and (3) $K(HCO_3)$.

and $NaNO_3$/γ-Al_2O_3 are more crystalline. The peaks ascribed to Li and Na aluminates are well observed on the corresponding XRD patterns together with those of γ-Al_2O_3 (Figs. 6 and 7).

The specific surface areas of the different samples are reported in Table 1. Loading the alumina supports with alkalines or Ca^{2+} cations induces a decrease of the surface areas. The magnitude of this effect is larger when γ-alumina is used as support with a 10-fold decrease. This decrease reveals a reaction between the basic salt and the acid γ-alumina with the formation of aluminates as shown by XRD patterns. By contrast, the limited decay of the surface of α-alumina upon alkaline loading shows a smaller reactivity, attributed to its lower reactivity with the alkalines.

The basic properties of the catalysts were determinated by calorimetry of CO_2 adsorption. The solid bases show moderate strengths with differentials heat of CO_2 adsorption within the range 90–115 kJ mol^{-1} (Fig. 8, Table 1). CsF and KF dispersed on α-Al_2O_3 shows basic sites with slightly stronger strength compared to the solid bases obtained by dispersion of Ca, Li and Na cations on γ-Al_2O_3. It is interesting to see that this basicity is only slightly affected by the choice of the cation, as reported in the calorimetric curves (Fig. 8). Note that γ-Al_2O_3 modified with Ca exhibits the highest total number of basic sites.

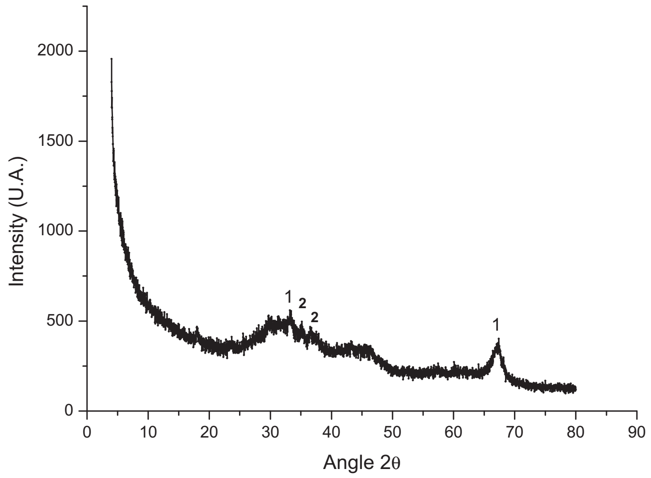


Fig. 5. DRX pattern of (a) $Ca(NO_3)_2$/γ-Al_2O_3-12, pre-treated 2 h at 723 K under air flow (1) Al_2O_3 and (2) $Ca_3Al_2O_6$.

Table 1
Specific surface areas and basicity features drawn from calorimetry of CO_2 adsorption.

Catalyst	Surface area (m^2/g)	Qdiff CO_2 adsorption[b] ($kJ\,mol^{-1}$)	Total basicity $Q_{diff} > 80\,kJ\,mol^{-1}$ ($\mu mol\,g^{-1}$)
$CsF/\alpha Al_2O_3$	6.3	115[a]	9
$KF/\alpha Al_2O_3$	7.8	110[a]	10
$Ca(NO_3)_2/\gamma Al_2O_3$	39.5	95[a]	55
$LiNO_3/\gamma Al_2O_3$	45.3	97[a]	32
$NaNO_3/\gamma Al_2O_3$	67.9	90[a]	34

[a] Mean differential heat of CO_2 adsorption at half CO_2 coverage.

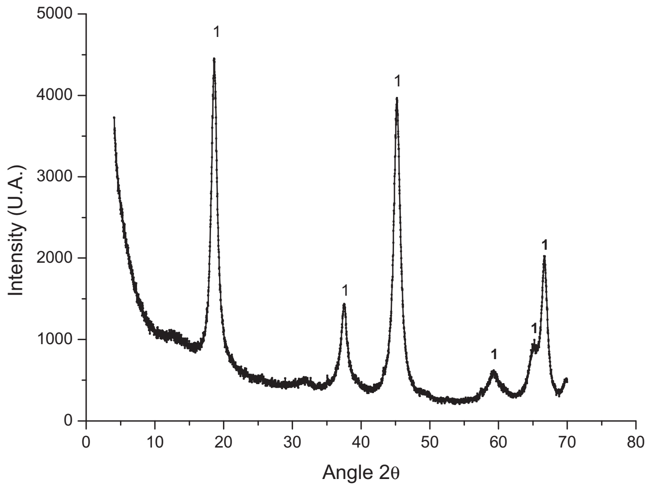


Fig. 6. DRX pattern of $LiNO_3/\gamma$-Al_2O_3-12, pre-treated 2 h at 723 K under air flow (1) $LiAlO_2$.

A smooth variation of the basic strength with the cation size was expected, which does not appear clearly in the present results. It has been proposed [14,15] that basic sites are indeed structural defects in which the coordination number of oxygen anions determines the basic strength. Changing the dispersion of the alkaline cations at the surface of the support most probably influences both the number of sites but also their strength. The reaction of the alkaline solution with the support produces then a complex solid.

The total acidity determined by TPD-NH_3 was expressed in mmol NH_3 adsorbed per g^{-1} and the estimation of the force of the acid sites was made in agreement with Yadav et al. [16]: the peak of ammonia desorption below 100 °C corresponds to the weak acid sites, that between 100 and 200 °C to the acid sites of moderate strength, that between 200 and 400 °C to the strong acid sites, and those responsible for desorption at $T > 400$ °C correspond to very strong acid sites (Table 2).

The catalysts $LiNO_3/\gamma Al_2O_3$ and $Ca(NO_3)_2/\gamma$-Al_2O_3 possess acid sites of medium strength with NH_3 desorption peaks at 157 and 187 °C, respectively. The catalyst $NaNO_3/\gamma$-Al_2O_3 possesses strong acid sites which release NH_3 at 390 °C. The total number of acid sites follows the order $NaNO_3/\gamma$-$Al_2O_3 > Ca(NO_3)_2/\gamma$-$Al_2O_3 > LiNO_3/\gamma$-$Al_2O_3$.

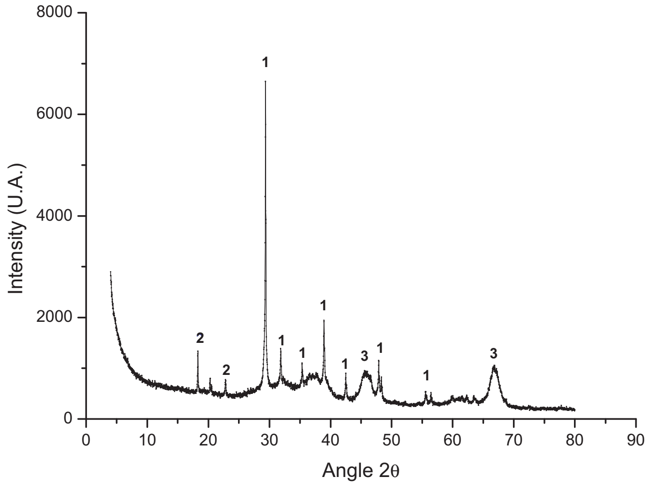


Fig. 7. DRX pattern of $NaNO_3/\gamma$-Al_2O_3-12, pre-treated 2 h at 723 K under air flow (1) $Na14Al_4O_{13}$, (2) $NaNO_3$, and (3) Al_2O_3.

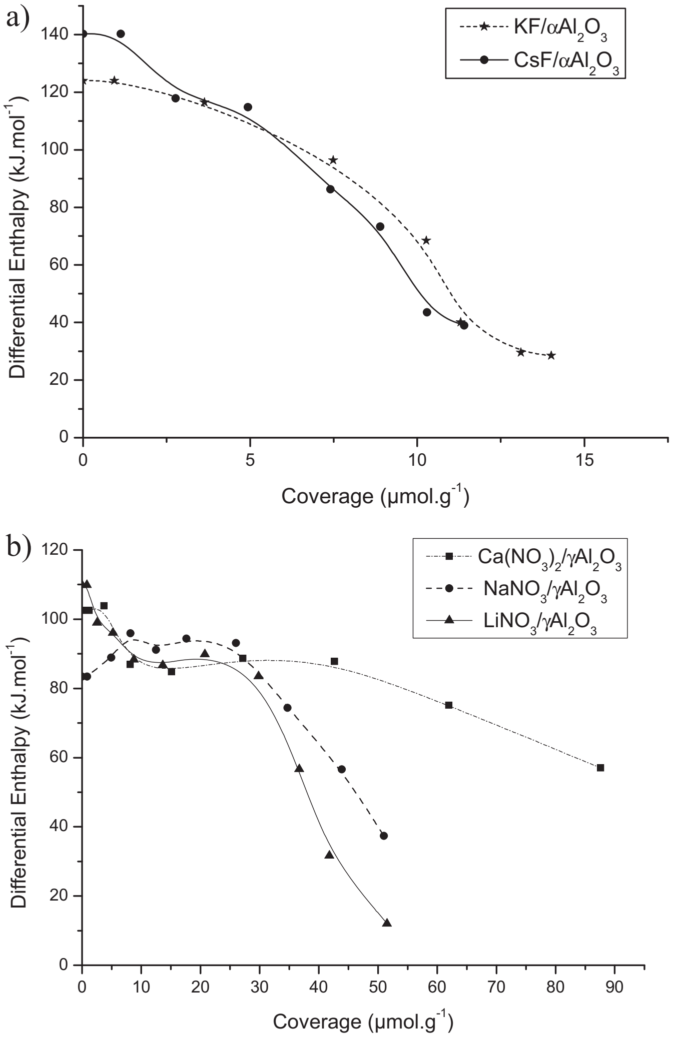


Fig. 8. Differential heats of adsorption of CO_2 on the solid bases used in this work. (a) CsF/α-Al_2O_3, KF/α-Al_2O_3, (b) $Ca(NO_3)_2/\gamma$-Al_2O_3, $NaNO_3/\gamma$-Al_2O_3, $LiNO_3/\gamma$-Al_2O_3.

Table 2
Acidic features of catalysts $LiNO_3/\gamma\text{-}Al_2O_3$, $NaNO_3/\gamma\text{-}Al_2O_3$ and $Ca(NO_3)_2/\gamma\text{-}Al_2O_3$.

Catalyst	T of NH_3 desorption (°C)	Acid strength	Total acidity mmol NH_3 g^{-1}
$LiNO_3/\gamma\text{-}Al_2O_3$	170	Moderate	0.237
$Ca(NO_3)_2/\gamma\text{-}Al_2O_3$	185	Moderate	0.577
$NaNO_3/\gamma\text{-}Al_2O_3$	390	Strong	1.032

3.2. Catalytic properties of solid bases in the reaction of ethyl acrylate transesterification with n-hexanol

First, an exploratory study was carried using $CsF/\alpha\text{-}Al_2O_3$ as catalyst. Two secondary products of Michael's addition of alcohols to the double bonds of the acrylates were identified in the reaction mixture (Scheme 2). These secondary products are formed in different amounts depending mainly on the catalyst and on the reaction extent. Their formation was favoured at higher conversion levels.

The addition of dimethylformamide (DMF) or 4-methylmorpholine (NMM) as solvent was investigated using $CsF/\alpha\text{-}Al_2O_3$ as catalyst at 353 K, with a ratio of reactants $R = 4$. The results are reported in Fig. 9. Dilution shows a marginal effect on the initial rate. $CsF/\alpha\text{-}Al_2O_3$ catalyst has shown to be active for both reactions, transesterification and Michael additions [11,13]. The Michael's reactions were favoured when a solvent was used, this already has been reported with $KF/\alpha\text{-}Al_2O_3$ catalyst [11] using DMF as solvent. The reaction accomplishment in absence of solvent allows a better control of secondary reactions and therefore high selectivity in transesterification products.

The effect of the molar ratio hexanol/acrylate was also investigated using ratios $R = 2$, 4 and 6. The results are reported in Fig. 10. It can be concluded that the molar ratio alcohol/acrylate influenced the activity of the catalyst but not the selectivities.

The effect of temperature was performed on the same catalyst. The results obtained for solvent-free reactions at 353, 373 and 403 K are reported in Fig. 11. At higher temperature, the conversion increased fast, which favoured the formation of the products of Michael's addition at the expense of the hexyl acrylate. From the result, the initial rate at low conversion was determined, which permits to determine an activation energy of 48.9 kJ mol^{-1} for the reaction of transesterification.

The distribution of basic sites in $KF/\alpha\text{-}Al_2O_3$ is very close to that of $CsF/\alpha\text{-}Al_2O_3$ with a slightly lower enthalpy of CO_2 adsorption

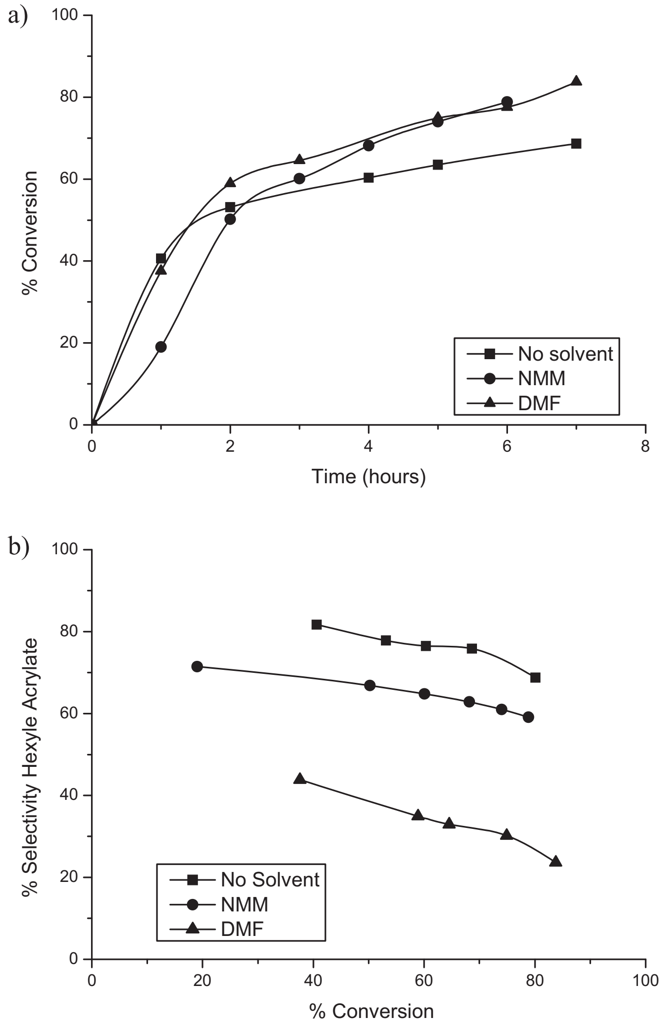


Fig. 9. Effect of solvent on the transesterification of ethylacrylate by n-hexanol. Catalyst: $CsF/\alpha\text{-}Al_2O_3$, $T = 353$ K, R hexanol/acrylate = 4. (a) Kinetic and (b) hexyl acrylate selectivity as a function of the conversion.

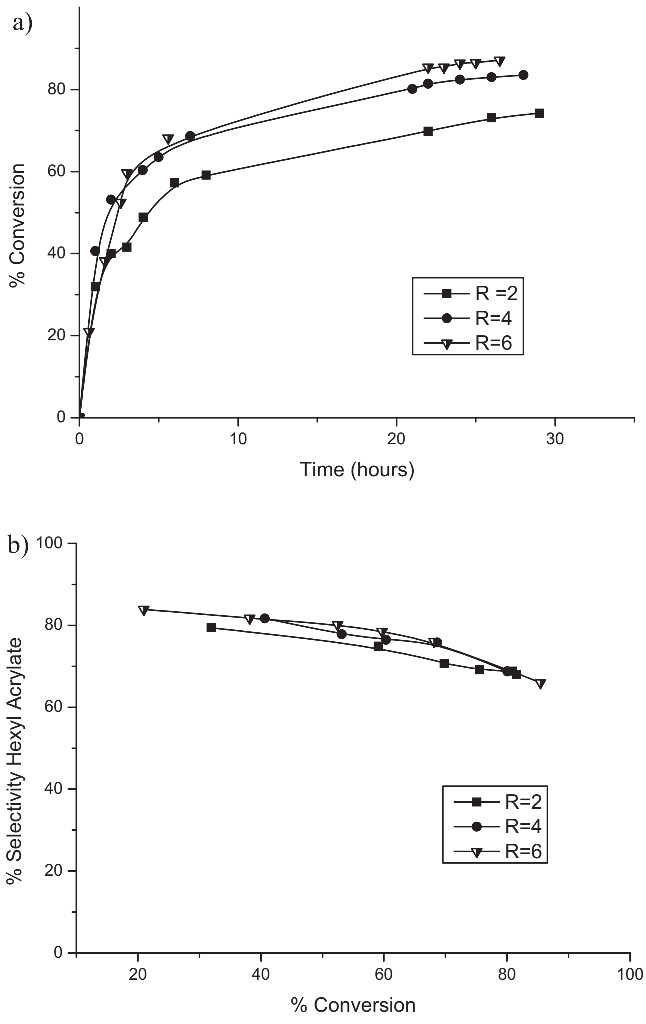
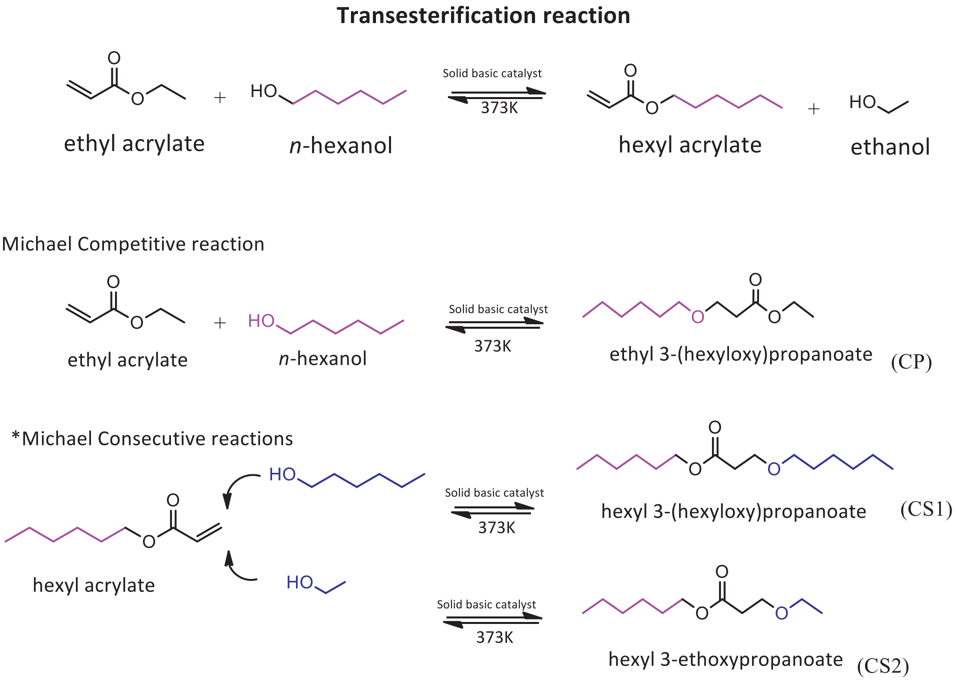


Fig. 10. Influence of the molar ratio hexanol/acrylate on the reaction of acrylate transesterification with hexanol. Catalyst: $CsF/\alpha\text{-}Al_2O_3$, $T = 353$ K, solvent-free. (a) Kinetics and (b) hexyl acrylate selectivity as a function of the conversion.



Scheme 2. Transesterification of ethyl acrylate with n-hexanol.

for the former one (Fig. 8). Their behaviour in the transesterification reaction of ethyl acrylate with n-hexanol (Table 3) shows that under the same conditions of reaction, the reaction is faster with KF/α-Al_2O_3 compared to CsF/α-Al_2O_3. Note that at equivalent conversion level, the selectivities are comparable.

The basic properties of CsF/α-Al_2O_3 and KF/α-Al_2O_3 have been previously compared in the reaction of condensation of organic carbonates with alcohols [9]. Both catalysts were active; reaching 100% conversion in 45 min and 5 h respectively for CsF/α-Al_2O_3 and KF/α-Al_2O_3. The authors attributed this distinct catalytic effect to the strongest basicity of CsF/α-Al_2O_3. Nevertheless, our results show an opposite effect; the CsF/α-Al_2O_3 leads to 49% conversion in 4 h whereas 15 min are enough with KF/α-Al_2O_3. These results suggest that the transesterification reaction of acrylates would be favoured by basic sites of weaker strength.

The series prepared *via* γ-Al_2O_3 modification with Ca, Li, Na are less active than KF/αAl_2O_3. $Ca(NO_3)_2$/γAl_2O_3 shows the lowest initial rate within the series however this solid base exhibits a remarkable high selectivity (>90%) up to a conversion level of about 60%. $NaNO_3$/γAl_2O_3 and $LiNO_3$/γAl_2O_3 are less selective than the Ca solid base whatever the conversion level (Fig. 12).

The catalyst $Ca(NO_3)_2$/γ-Al_2O_3 is characterized by a larger number of basic sites with lower force compared with $LiNO_3$/γ-Al_2O_3 and $NaNO_3$/γ-Al_2O_3. The catalytic properties are illustrated in Table 4, the reaction time to reach 31% conversion are 5, 3 and 1 h, respectively. In this case, the results do not allow us to reach a conclusion relative to the influence of basic properties on the catalytic behaviour.

One can recall that γ-Al_2O_3 loaded with alkali metal salts has been used for the transesterification of vegetable oils with methanol. In that case, the catalytic properties were correlated with basicity [17]. K/Al_2O_3 was the most active catalyst, but recyclability was not investigated. In the case of Na/Al_2O_3 a leaching of Na has been reported [18].

The reaction pathways on these catalysts, initiated by the proton abstraction from the alcohol by the basic sites to generate the alkoxide RO^- has been well established and is not the milestone. Then, the alkoxide can attack the carbonyl of the ester function

Table 3
Catalytic properties of CsF/α-Al_2O_3 and KF/α-Al_2O_3 in the transesterification reaction of ethyl acrylate with n-hexanol, $T = 353$ K, m.cat/m.acryl. = 6%, $R = 2$, solvent-free.

Catalyst	Time (h)	Conversion (%)	Selectivity (mol%)		
			Hexyl acrylate	CP[a]	CS1[a]
KF/α-Al_2O_3	0.25	49	86	11	3
CsF/α-Al_2O_3	4.0	49	80	15	5

[a] CP, ethyl 3-(hexyloxy)propanoate; CS1, hexyl 3-(hexyloxy)propanoate.

Table 4
Catalytic properties of $LiNO_3$/γ-Al_2O_3, $NaNO_3$/γ-Al_2O_3 and $Ca(NO_3)_2$/γ-Al_2O_3, in the transesterification reaction of ethyl acrylate with n-hexanol, $T = 353$ K, m.cat/m.acryl. = 6%, $R = 2$, solvent-free.

Catalyst	Time (h)	Conversion (%)[a]	Selectivity (mol%)		
			Hexyl acrylate	CP[a]	CS1[a]
$Ca(NO_3)_2$/γ-Al_2O_3	5	32	97	3	0
$LiNO_3$/γ-Al_2O_3	3	38	76	20	4
$NaNO_3$/γ-Al_2O_3	1	33	85	12	3

[a] CP, ethyl 3-(hexyloxy)propanoate; CS1, hexyl 3-(hexyloxy)propanoate.

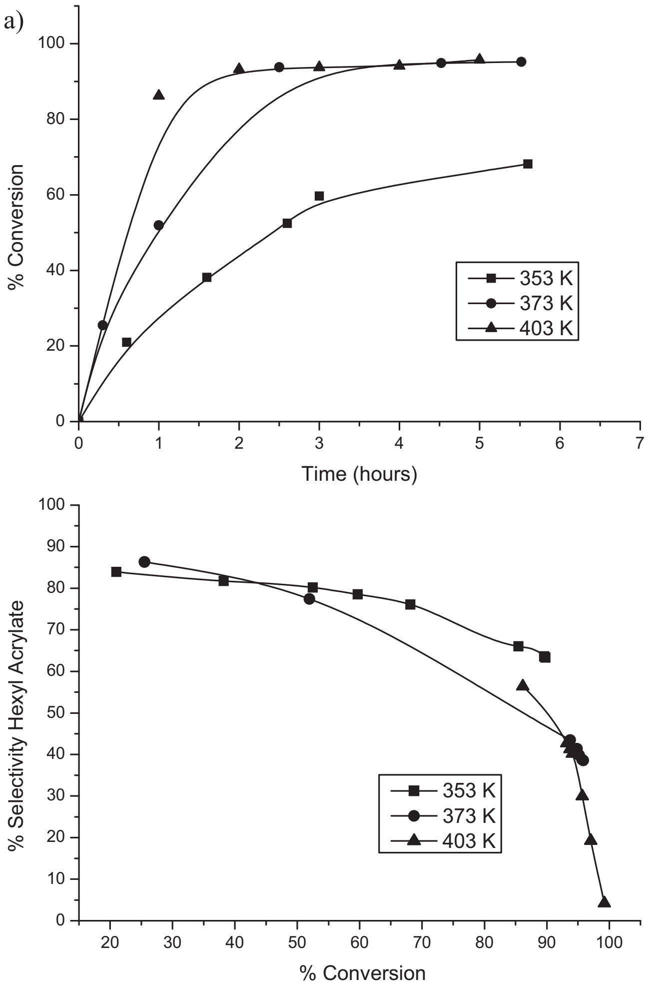


Fig. 11. Influence of the temperature on the reaction of acrylate transesterification with hexanol. Catalyst: CsF/α-Al_2O_3, $R=6$, (a) kinetics, and (b) hexyl acrylate selectivity as a function of the conversion.

(transesterification reaction), which could be polarized by the acid sites. This could make the transesterification easier. In the literature, transesterification is much slower on acids than on basic sites in the case of vegetable oils with methanol [19-21]. When longer alcohols are concerned, such as ethanol, this is the contrary due to lower acidity of longer alcohol compared to methanol. Thus, one can anticipate that the rate of the transesterification and its selectivity should depend both on the basic and on the acid properties of the solid catalyst. The alkoxide derived from hexanol or ethanol can also attack the double bond in the vinyl group of the acrylate (Michael reaction), which could also depend on polarization effects due to the influence of the acid sites present on the surface. At this point, it seems that electronic factors are determinants to favour one or the other reaction, then the size and charge of the metal cation become important to consider.

The results show that Ca^{2+} promotes the reaction of the alkoxide with ethyl acrylate carbonyl group, providing high selectivity to hexyl acrylate. The measurement of the acidic properties allows to establish a relationship in the following order: $Na^+ \geq Ca^{2+} > Li^+$. The order of selectivities in transesterification Ca/γ-Al_2O_3 > Na/γ-Al_2O_3 > Li/γ-Al_2O_3, which fits with the order of basicity of the samples.

Finally, recycling was investigated on the most selective catalyst $Ca(NO_3)_2$/γ-Al_2O_3. The procedure used for this was the removal, after 1 h of reaction, of the liquid phase with a syringe avoiding exposure to air, followed by the introduction of a new charge of

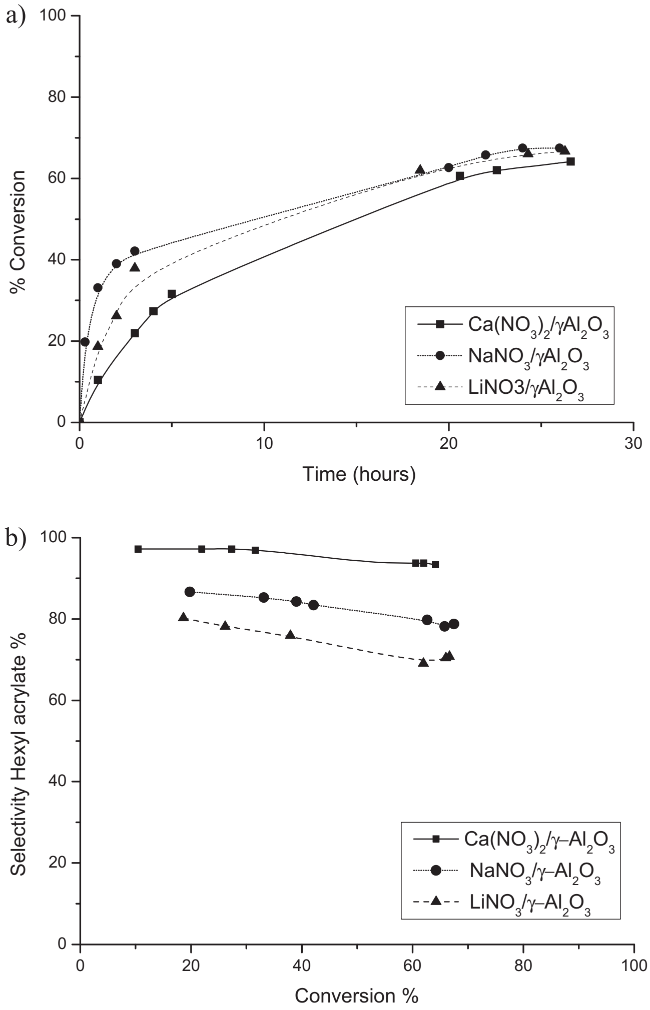


Fig. 12. Transesterification reaction of ethyl acrylate with n-hexanol on Ca, Li, Na/γ-Al_2O_3. $T=353$ K, mcat/m.acryl. = 6%, $R=2$, solvent-free, (a) kinetics, and (b) hexyl acrylate selectivity as a function of the conversion.

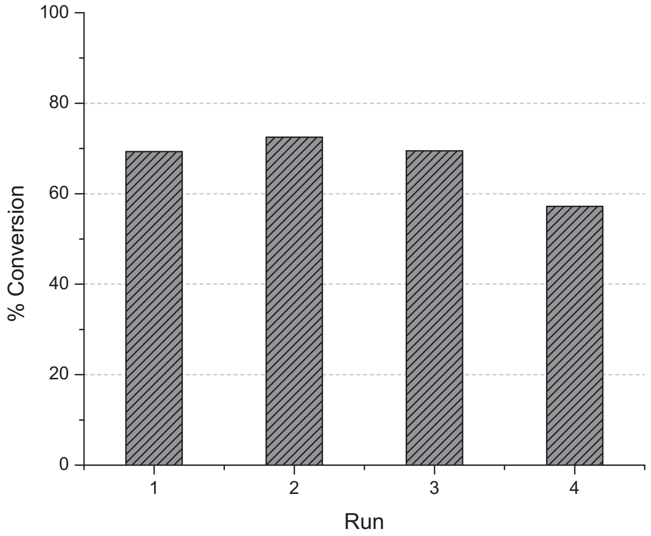


Fig. 13. Recycling of Ca/γAl_2O_3 catalyst (reaction time: 1 h). Reaction conditions: mcat/m.acryl. = 6%, solvent-free, 373 K, $R=1$.

reactants. In this case, in order to avoid any effect of water vapour in the process, the reactor was flushed by a small stream of dry nitrogen. The results obtained with this procedure are reported in Fig. 13. As can be seen, the activity dramatically increases since the conversion reached after 1 h is the same as that measured before after 24 h, with the same selectivity, showing that trace amounts of water vapour deactivate the catalyst. Moreover, this catalyst could to be recycled up to 4 cycles without any loss of selectivity. The decrease in the conversion observed after 4 cycles could be due in part to the recycling procedure where catalyst loss may occur.

4. Conclusions

Basic catalysts Li(Na,Ca)/γ-Al_2O_3 or KF(CsF)/α-Al_2O_3, tested in the transesterification reaction of ethyl acrylate with n-hexanol, were shown to be active and selective. Results suggest that the transesterification reaction of acrylates would be favoured by basic sites of weakest strength and side reactions of Michael additions occur and are favoured on the strong basic sites. The reaction may be carried out under mild conditions, in solvent free conditions and with a stoichiometric ratio of reagents, obtaining high selectivities in hexyl acrylate (>90%) at high conversion (>60%) within 1 h of reaction with $Ca(NO_3)_2$/γ-Al_2O_3 as catalyst. This catalyst could be reused up to 4 cycles without significant changes in ethyl acrylate conversion.

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