Catalysis Letters 43 (1997) 139–142

Homogeneous and supported titanates as catalysts for transesterification of acrylic esters

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Received 22 July 1996; accepted 29 October 1996

The transesterification of methylmethacrylate with 1-dodecanol has been studied by using Brønsted acid and Lewis acid type catalysts either for homogeneous or heterogeneous systems. Initial rates studies in a batch reactor lead to a greater efficiency for the Lewis acid catalysts (soluble or supported titanates). The activity of the supported catalyst can be linked to the molecular association of the titanates during the fixation on the silica support, the existence of monomeric species corresponding to the most important activity. The nature of the support has also an influence: for the same density of titanium atoms, a smaller surface area leads to a better efficiency.

Keywords: transesterification, supported titanate, kinetics

1. Introduction

Titanates have been extensively employed as homogeneous catalysts for esterification and transesterification because they favour high conversion rates with production of esters of high molecular weights and very low acid numbers.

In a previous work, we studied the esterification of stearic acid with low boiling alcohols in a semi-continuous reactor using homogeneous titanates as catalysts [1]. The kinetic studies at high temperature (160°C), for which titanates are more efficient, required to take in account the uncatalyzed reaction; the found order of 0.5 with respect to the catalyst suggested the existence of an equilibrium between a monomeric and a dimeric titanium compound, the dimer being prevalent and inactive at low temperature.

For the esterification of stearic acid with isopropyl alcohol, we also investigated the effect of the fixation of titanates on alumina or silica supports in order to avoid elimination of the catalyst by hydrolysis and filtration at the end of the reaction [2]. This heterogenized catalyst led to a better efficiency than the homogeneous system and can be recovered and recycled provided that a few precautions be taken.

We used the supported titanates in transesterification to facilitate the kinetic measurements because, contrary to the esterification reaction, the transesterification without catalyst is impossible below 120°C. In a previous work [3] we have clearly established the rate law $r = k$ [alcohol] [ester][catal] in the case of the ethyl propionate–1-dodecanol system. The order 1 with respect to the catalyst facilitated the study of the influence of the titanium environment on the reactivity of the catalyst. From the kinetic equation, we proposed a typical Lewis acid mechanism corresponding to successive additions of ester and then alcohol.

The present work describes extension of this study to the transesterification of a vinylic ester (methyl methacrylate, or MMA) with 1-dodecanol, with the aim to compare the efficiency of Brønsted acid catalysts such as sulfuric acid or sulfonic resin, with Lewis acid catalysts such as titanates either for homogeneous system or heterogeneous systems.

2. Experimental

The silica supports (Rhne-Poulenc SPH 540 and Degussa MOX 80, specific surface area 277 and 80 m^2 g^{-1}) were previously dried at 160°C under 10^{-4} Torr for 18 h. The acid strengths were estimated by amine titrations [4]. We found: $3.3 < H_0 < 4.8$ for SPH 540 and $H_0 < 3.3$ for MOX 80. Acidic ion exchange resin Amberlyst 15 Fluka (45 m^2 g^{-1}; 4.6 meq H^+/mg) was previously dried at 80°C under vacuum for 18 h.

The supported titanates were obtained according to the following reaction:

$$\mathrm{TiX(OiPr)_3 + HO{-}[Si] \rightarrow [Si]{-}O{-}Ti(OiPr)_3 + HX}$$

with X = CH_3, Cl, OiPr, using toluene as solvent. The reaction was followed by measuring volumetrically the gas production (such as 0.9 CH_4/Ti). The presence of $[Si]{-}O{-}Ti(OiPr)_3$ units was confirmed by ^{13}C NMR on the solid or by exchange reaction of the isopropoxy group with a heavy alcohol [2]. The titanium titrations on the solids were carried out as described elsewhere [3].

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Transesterifications were carried out in a batch reactor, at low temperature (58°C), using initial kinetic conditions as described earlier [3]; this allows to minimize the exchange reactions of the catalyst with alcohol and ester. We used stoichiometric amounts of ester and alcohol (2.9 mol ℓ^{-1}) and concentrations of 10^{-3} mol ℓ^{-1} for the soluble catalyst and of 50 gℓ^{-1} for the supported catalyst. Molecular sieve was added with a concentration of 50 g ℓ^{-1} to avoid the extreme sensitivity of the catalyst to hydrolysis.

The formation of dodecyl methacrylate was followed by GC analysis, using dodecane as internal reference and the conversion values X (%) were calculated as a function of time.

We checked that, under the same experimental conditions, there was no catalytic effect due to the silica supports (X staying near 0%).

3. Results and discussion

Measurements of the reaction rates using initial kinetic studies, for which the conversion X is a linear function of time, allow easy obtaining of the experimental rate constants. Conversion values X remain linear functions of time, as far as $X < 15\%$, during the first 6 h of the reaction.

3.1. Homogeneous catalysis: Brønsted acid and Lewis acid type catalysts

Using the same initial kinetic conditions, we compared the activities of two Brønsted acid type catalysts, such as sulfuric and methanesulfonic acids, with a Lewis acid type catalyst such as tetraisopropyltitanate. The two Brønsted acids produce comparable activities (fig. 1) with rate constants close to 1.2×10^{-5} mol^{-2} ℓ^2 s^{-1} (table 1). The rate law $r = k$[alcohol][ester][catal], previously established for the transesterification of ethyl propionate [3], was supposed to be identical for this system.

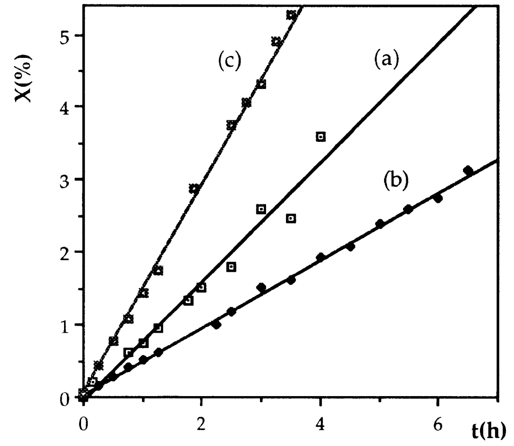

Fig. 1. Homogeneous system: conversions (%) versus time (h) in a batch reactor at 58°C with [alcohol] = [ester] = 2.9 mol ℓ^{-1} and with catalysts (a) [H_2SO_4] = 69×10^{-3} mol ℓ^{-1}, (b) [HSO_3CH_3] = 34×10^{-3} mol ℓ^{-1}, (c) [Ti(OiPr)$_4$] = 2×10^{-3} mol ℓ^{-1}.

With the Lewis acid type catalyst, we first checked the order relative to the catalyst. By using three different amounts of titanate (1.20×10^{-3}, 2.05×10^{-3} and 4.65×10^{-3} mol ℓ^{-1}), and from the slopes of the straight lines, we determined the rates $r = 11.98 \times 10^{-6}$, 23.80×10^{-6}, and 50.52×10^{-6} mol ℓ^{-1} s^{-1}.

The linear variation of the conversion X with time (fig. 1) indicates that, for the initial kinetic conditions, the environment of titanium is not modified by exchange reactions with the reagents. The order 1 with respect to the catalyst indicates that Ti(OiPr)$_4$ exists as a prevailing monomer form in this system.

Indeed, for concentrations below 10 mmol ℓ^{-1}, isopropyl titanate is known to exist as a monomeric form [5]. We already showed that, for higher concentrations (10^{-2} to 10^{-1} mol ℓ^{-1}), the order with respect to the titanate becomes fractional and close to 0.5 [1].

The same rate law may thus be written as $r = k$[alcohol][ester][catal], and thereupon an experimental rate constant $k = 111.8 \times 10^{-5}$ mol^{-2} ℓ^2 s^{-1} can be estimated (table 1). The Lewis acid catalyst thus presents an activity one hundred times greater than the Brønsted acid catalysts.

The apparent energy of activation was calculated for [Ti(OR)$_4$] (1.2×10^{-3} mol ℓ^{-1}) by using three different temperatures: 58.5, 62.5 and 69.5°C. We obtained initial rates $r = 119.8 \times 10^{-6}$, 15.30×10^{-6} and 28.23×10^{-6} mol ℓ^{-1} s^{-1}, corresponding to an activation energy $E_A = 75 \pm 5$ kJ mol^{-1}.

3.2. Heterogeneous catalysis

Using the same initial kinetic conditions for all experiments, we compared the activity of an acidic ion exchange resin (Amberlyst 15) with that of the supported titanate [Si]-Ti(OiPr)$_3$ containing 9 mg Ti/g.

From the results reported in table 1, it is apparent that the activity of the supported titanate is about ten times lower than the soluble one, but still, the Lewis acid catalyst is more efficient than the Brønsted acid one (Amberlyst resin), as was previously observed for the homogeneous catalysis.

We thought it possible to increase the activity of the

Table 1
Rate constants for homogeneous and heterogeneous systems. $k \times 10^5$ (mol^{-2} ℓ^2 s^{-1})

Homogeneous system			Heterogeneous system	
H_2SO_4	CH_3SO_3H	Ti(OiPr)$_4$	Amberlyst 15	[Si]–O–Ti(OiPr)$_3$
1.1	1.3	111.8	0.3	8.0

resin by addition of Lewis acid sites as was observed in the case of the addition of $AlCl_4$ or BF_3 [6]. Considering the results of homogeneous catalysis, it could be considered that, by substituting $Ti(OR)_3$ groups for H^+ acid sites of the resin, one could increase the catalytic activity of the resin. We carried out a first grafting corresponding to 8 mg Ti/g (or 2.23 Ti/nm^2) without observing any gain of activity (r varying from 12.2×10^{-6} to 11.6×10^{-6} mol ℓ^{-1} s^{-1}). We then decided to substitute more Brønsted acid sites of the resin by increasing the density of titanium atoms and using for that a grafting corresponding to 18 mg Ti/g or 5.0 Ti/nm^2.

Since metallic centers were too close to each other, we observed a decrease in activity ($r = 3.7 \times 10^{-6}$ mol ℓ^{-1} s^{-1}). This phenomenon can be compared to an increase in the titanium concentration in the homogeneous system which would lead to a predominance of dimeric species and thus a decreasing catalytic activity.

The apparent activation energy of the heterogenized system was calculated by using four different temperatures (fig. 2). We obtained the initial rates $r = 6.73 \times 10^{-6}$ mol ℓ^{-1} s^{-1} for 59.2°C; $r = 9.65 \times 10^{-6}$ mol ℓ^{-1} s^{-1} for 61.6°C; $r = 14.33 \times 10^{-6}$ mol ℓ^{-1} s^{-1} for 71.3°C and $r = 36.81 \times 10^{-6}$ mol ℓ^{-1} s^{-1} for 79.0°C, corresponding to $E_A = 75 \pm 5$ kJ mol^{-1}. This value is fully comparable to the value obtained for the transesterification of ethyl propionate ($E_A = 90 \pm 5$ kJ mol^{-1}). This allows us to propose, for the transesterification of MMA, a similar Lewis acid mechanism with successive additions of ester and alcohol [3].

3.2.1. Influence of the molecular association of titanates

Different titanates $TiX(OiPr)_3$ with $X = CH_3$, Cl, OiPr, were fixed on SPH 540 in such a way that the concentration of catalyst is near 10^{-2} mol ℓ^{-1} and the titanium concentrations all identical (9–9.5 mg Ti/g). The corresponding transesterification reactions of MMA lead to extremely variable initial rates per titanium atom (table 2), the most important activity corresponding to the methylated compound.

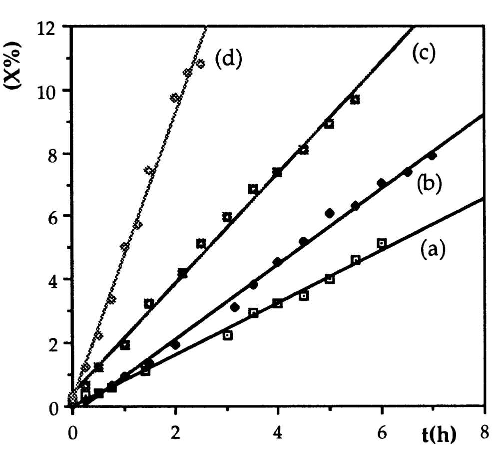

Fig. 2. Heterogeneous system: conversions (%) versus time (h) in a batch reactor with [alcohol] = [ester] = 2.9 mol ℓ^{-1}, [sieve] = 50 g/ℓ and [catal] = 50 g/ℓ of SPH 540 silica containing 9 mg Ti/g at (a) 59.2°C; (b) 61.6°C; (c) 71.3°C; (d) 79.0°C.

It is possible to link the observed variations of activity to the molecular association of titanates in toluene solution during the fixation on the support; the association by alkoxy linkages depends on steric and electronic factors. It is thus known that such titanium compounds exist in benzene solution as both monomeric and dimeric forms in equilibrium: the monomer form is preponderent in the case of the methylated compound $CH_3Ti(OiPr)_3$ [7], whereas the dimer forms are prevailing in the case of $TiCl(OiPr)_3$ and $Ti(OiPr)_4$ [8].

The predominance of monomeric species in the toluene solution during the fixation of titanate on the support should result in a large number of titanium atoms possessing a vacant site during the catalysis of transesterification and, thus, in a higher r/Ti activity. We checked this assumption by using a dilute solution of $Ti(OiPr)_4$ (close to 5×10^{-3} mol ℓ^{-1}), thereby favouring the presence of monomeric species. Under such conditions, the activity increases from 1.7×10^{-4} to 6.2×10^{-4} mol atom^{-1} s^{-1} (table 2). This activity becomes comparable with that obtained for the fixation of monomeric compounds, in so far that hydrolysis of the catalyst is facilitated by these conditions, i.e., when using a large amount of solvent, and should result in an apparent decrease in the activity during the kinetic measurements.

3.2.2. Influence of the specific surface area of the support

The influence of the specific surface area of the support was evaluated by using a MOX 80 silica which, possessing a smaller surface area and thus bigger pores than SPH 540, should have led to a better efficiency for the same density of titanium. It is clear from fig. 3, that the three fixations of $TiCl(OiPr)_3$ corresponding to 2.53, 6.25 and 24 mg Ti/g lead to a decrease of r/Ti values: 22.9×10^{-4}, 9.34×10^{-4} and 1.08×10^{-4} mol atom^{-1} s^{-1}, respectively. The efficiency of the catalyst fixed on the MOX 80 support keeps on decreasing while the density of titanium atoms increases. One might think that this process is due to the surface interactions between two neighbouring metallic centers when they are too close to each other. Indeed if a homogeneous distribution of titanium on the surface is supposed, a density close to 1 Ti/nm^2 corresponds to a distance between the

Table 2
Activity values obtained for different titanates

Titanate	r/Ti 10^4 (mol atom^{-1} s^{-1})
$TiCH_3(OiPr)_3$	7.0
$TiCl(OiPr)_3$	4.9
$Ti(OiPr)_4$	1.7
diluted[a] $Ti(OiPr)_4$	6.2

[a] Concentration close to 5×10^{-3} mol ℓ^{-1}.

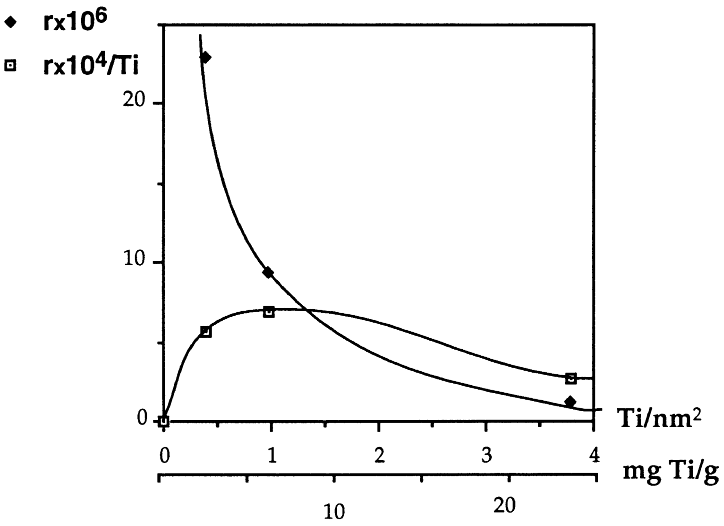

Fig. 3. Reaction rates r (10^6 mol ℓ^{-1} s^{-1}) and activities r/Ti (10^4 mol atom^{-1} s^{-1}) versus titanium density (Ti/nm^2 and mg Ti/g) with silica MOX 80 at 58°C.

atoms estimated at 1 nm. On the other hand, a comparison of efficiency with the homogeneous system is more favorable to this latter. Indeed, for a same number of titanium atoms in the reactor for example 2 g of silica with 2.53 mg Ti/g, the r/Ti value (22.9×10^{-4} mol atom^{-1} s^{-1}) remains smaller than the value calculated for the equivalent monomer titanate in homogeneous catalysis ($r/\mathrm{Ti} = 109 \times 10^{-4}$ mol atom^{-1} s^{-1} for $2.64 \times 10{-}3$ mol ℓ^{-1} solution).

For a same titanium density close to 0.5 Ti/nm^2, the efficiency of MOX 80 is more than three times larger than SPH 540 ($r/\mathrm{Ti} = 4.9 \times 10^{-4}$ mol atom^{-1} s^{-1}).

The optimal grafting, i.e., the appropriate quantity (mass or surface) of titanium to be fixed in order to obtain a maximum reaction rate r, can be seen from fig. 3, in which the higher r value corresponds to a density close to 1.1 Ti/nm^2 (or 7 mg Ti/g).

When considering possible industrial applications, the mechanical properties of SPH 540 silica make its use more interesting in spite of its lower efficiency. Therefore, we checked the stability of the $CH_3Ti(OiPr)_3$ titanate supported on SPH 540 silica, by heating at 200°C under argon pressure (3.5 bar) for 45 h. Subsequent titanium titrations on the liquid phase (4 ppm) show the strong stability of the Si–O–Ti bond at the surface of the solid.

4. Conclusion

This work allowed us to demonstrate that, in the homogeneous catalysis of transesterification of vinylic esters, the Lewis acid type catalysts possess a greater efficiency than the Brønsted acid type catalyst. However, difficulties arise as a consequence of the existence of a dimeric inactive form of the catalyst for high concentrations.

In the heterogeneous catalysis, the Lewis acid type catalyst demonstrates a greater efficiency than the Brønsted acid one. Indeed, supported titanium catalysts are more active if dimerisation of the soluble titanium precursors is prevented during the fixation on the support, either by using a monomeric precursor in solution or by working with a sufficiently low concentration to favour the formation of a monomeric active form.

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