

Polymer-supported titanates as catalysts for transesterification reactions

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Polymer-supported titanates were prepared by covalent bonding of a trialkoxychlorotitanate to a preformed macroporous poly(4-hydroxystyrene) resin. The reactivity and stability to recycling of the catalyst obtained were demonstrated in the catalysis of the transesterifications of methyl methacrylate with 2-ethylhexanol and ethyl butyrate with 1-dodecanol. A low leaching of titanium was observed during four successive uses of the resin as a transesterification catalyst. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Transesterification is a useful reaction for the chemical modification of monomers, polymers or copolymers bearing ester groups¹. Although transesterification can be catalysed by both bases and acids, including polymeric acids², the most commonly used catalyst is dibutyltin oxide³. However, the toxicity of this species is a major drawback for its further exploitation⁴. There is therefore a need for new organometallic transesterification catalysts.

Titanates have been employed as homogeneous catalysts in esterifications and transesterifications due to their high selectivity⁵. However, their removal by hydrolysis and filtration at the end of the reaction is often tedious. Alkyl titanates exist in solution as monomeric species in equilibrium with dimers, the latter form being inactive as a catalyst⁶. Titanates immobilised on an insoluble support could be easily recovered by simple filtration, thus avoiding the hydrolysis step and leading to a simpler work-up⁷.

Furthermore, it might be expected that the 'site isolation' brought about by the relatively rigid network of the support would inhibit oligomerisation of the bound titanate moieties. This might lead to an increase in the concentration of 'monomeric' species and hence to increased activity in the immobilised catalyst. In this context alkyl titanates have been already grafted onto silica and used as heterogeneous catalysts for transesterification with good efficiency⁸.

With this in mind, we decided to attach covalently an alkyl titanate to a macroporous poly(4-hydroxystyrene-co-divinylbenzene) resin. The resulting polymer-supported titanate was then used as a transesterification catalyst, with special emphasis on the activity, metal leaching and the recycling behaviour of the catalyst.

EXPERIMENTAL

Material

All the monomers (styrene (S), divinylbenzene (DVB),

p-acetoxystyrene (AS)) and other components involved in the polymerisation (azobisisobutyronitrile (AIBN), 2-ethylhexanol, suspension stabilisers) were used as received. Chloro-tri-isopropoxy titanium (Acros), tetraisopropoxy titanium (Aldrich), and titanium tetrachloride (Aldrich) were used without further purification. 2-ethylhexanol and 1-dodecanol used in transesterifications were distilled over CaH₂ and stored over molecular sieves. All solvents were dried according to published procedures.

Synthesis of macroporous poly(4-acetoxystyrene-co-styrene-co-divinylbenzene) beads (ACP)

The suspension polymerisation was performed in a parallel-sided glass reactor already described in the literature⁹. The organic phase was composed of the comonomers (15 cm³) (see Table I), AIBN (1.31 g) as the initiator and 2-ethylhexanol (15 cm³) as the porogen. The mixture was suspended in water (240 cm³) containing a suspension stabiliser (a mixture of gelatin and poly(diallyldimethylammonium chloride) (high molecular weight grade as a 20% aqueous solution)). The polymerisation was performed at 80°C for 8 h after which the resulting spherical particles were washed with water, ethanol, acetone and dried under vacuum.

Conversion of ACP to poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) beads (HP)

Polymeric particles with a diameter between 200 and 500 μm were hydrolysed. In a typical experiment, the resin beads (10 g) were suspended in dioxane (200 cm³); hydrazine hydrate (40 cm³) was then added and the reaction medium mechanically stirred for 2 days at 80°C. Then, aqueous HCl was added and the beads were washed successively with water, ethanol, acetone, ether and vacuum dried. For further use, residual water traces were removed by azeotropic distillation with toluene using a Dean–Stark apparatus for 2 days. Since the polymeric hydroxystyrene is somewhat hygroscopic, the particles were stored in toluene.

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Table 1 Characteristics of macroporous poly(4-acetoxystyrene) resins

Polymer	Monomer composition AS/S/DVB	Resin yield (%)	Particle size distribution (μm)				
			> 800	800–500	500–315	315–200	< 200
ACP1	10/70/20	77	4	3	23	34	36
ACP2	27/53/20	90	33	39	20	4	4
ACP3	40/40/20	94	14	14	57	9	6
ACP4	50/30/20	95	21	27	40	5	7

Table 2 Characteristics of the resins functionalised by Methods A and B (see text)

Starting resin	Theoretical phenol loading (mmol/g) ^a	Grafted support	Theoretical loading Ti (mmol/g) ^b	Measured loading Ti (mmol/g) ^c	Measured loading Cl (mmol/g) ^d	Measured Cl/Ti molar ratio	Degree of grafting (%) ^e
HP1	1.0	TiP1	0.7	0.36	0.14	0.4	51
HP2	2.9	TiP2(I)	1.3	0.92	0.91	1.0	72
HP2	2.9	TiP2(II)	1.3	0.81	0.81	1.0	62
HP3	4.2	TiP3	1.6	0.63	0.38	0.60	24
HP4	5.1	TiP4	1.8	1.30	0.32	0.25	18

^aestimated from comonomer feed ratios

^bestimated from theoretical phenol loading

^cdetermined from Ti analysis

^ddetermined from Cl analysis

^ecalculated from measured Ti and theoretical Ti contents

Attachment of ClTi(OCH(CH₂Cl)CH₃)₃ to poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) beads (HP)

Two methods were used to synthesize ClTi(OCH(CH₂Cl)CH₃)₃:

Method A: Preparation of resin TiP2(I). Tetraisopropyl titanate (11.4 g, 40 mmol), chloropropan-2-ol (15.1 g, 160 mmol mixture of isomers containing up to 25% of 2-chloropropanol), and toluene (200 cm³) were stirred together. The azeotrope toluene/isopropyl alcohol (b.p. 80.6°C) was slowly distilled until the temperature at the top of the column reached 110°C. The remaining solvent was withdrawn under reduced pressure and the residual brown viscous solid analysed (elemental microanalysis (wt%) found: Ti: 11.7; Cl: 31.0, Cl/Ti: 3.6; calculated Ti: 11.35; Cl: 33.66).

The crude product (3.2 g, 7.5 mmol) was dissolved in chloroform (50 cm³) in a two-necked round-bottomed flask. The solution was cooled to 0°C and TiCl₄ slowly added under nitrogen. The reaction was left at room temperature for 4 h. The mixture was then injected into a suspension containing HP2 resin (4 g, 11.6 mmol phenoxy groups) and triethylamine (1.2 g, 12 mmol) in chloroform (100 cm³). The reaction was left for 3 days at room temperature after which the resulting orange-yellow resin beads TiP2(I) were filtered off and continuously extracted for 2 days with chloroform using a Soxhlet apparatus, and then dried under vacuum (titanium content: 1.3 mmol/g). TiP1 resin was prepared from HP1 resin using the same protocol.

Method B: Preparation of resin TiP2(II). Powdered activated 3Å molecular sieves (75 g, 2 days at 220°C), ClTi(OiPr)₃ (3.9 g, 15 mmol) and 1-chloropropan-2-ol (5.7 g, 60 mmol) were mixed together at 70°C for 4 h in chloroform (200 cm³) under nitrogen. The mixture was then filtered under nitrogen and the molecular sieves washed with chloroform (50 cm³). The resulting solution was then injected into a suspension containing resin HP2 (5 g, 14.5 mmol phenoxy groups) and triethylamine (1.5 g,

15 mmol) in chloroform (100 cm³). The reaction proceeded similarly to that described above to yield resin TiP2(II) (titanium content: 0.81 mmol/g). TiP3 and TiP4 resins were prepared from resins HP3 and HP4, respectively, using the same protocol.

Transesterification of methyl methacrylate (MMA) with 2-ethylhexanol

In a typical procedure, resin TiP2(II) (2 g, 1.6 mmol Ti) was suspended in a 50 mL three-necked round-bottomed flask containing methyl methacrylate (22.53 g, 225 mmol), 2-ethylhexanol (14.64 g, 112 mmol) and diphenyl picryl-hydrazyl hydrate (40 mg, 0.1 mmol) as polymerisation inhibitor. The suspension was degassed and then heated at 115°C or 130°C for 24 h after which the resin beads were filtered off, washed several times with chloroform and dried under vacuum for further use (the titanium content was analysed after each reaction). The remaining methyl methacrylate was extracted from the liquid phase by distillation under vacuum. Then 2 g of the solution were passed through a silica gel column to recover the ester formed (20 g SiO₂, eluant: ether/petroleum ether: 1/40).

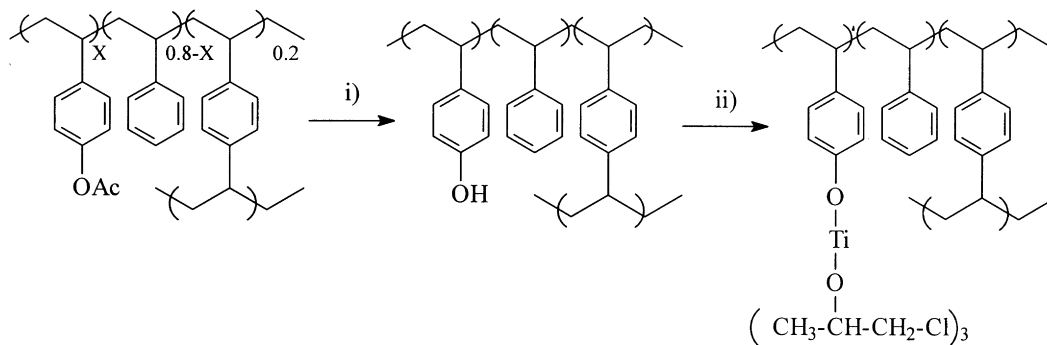
Transesterification of ethyl butyrate with dodecanol

Ethyl butyrate (9.93 g, 85.5 mmol), dodecanol (15.93 g, 85.5 mmol), decane (0.717 g, 5 mmol) as internal reference for GC analysis and resin TiP2(II) (1.5 g, 1.2 mmol Ti) were suspended in a 50 mL three-necked round-bottomed flask. The suspension was degassed and heated at 115°C for 48 h. The conversion was then determined via GC. The resin beads were filtered off and continuously extracted for 24 h with chloroform using a Soxhlet apparatus. The titanium content was then determined.

RESULTS AND DISCUSSION

Preparation of macroporous poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) beads

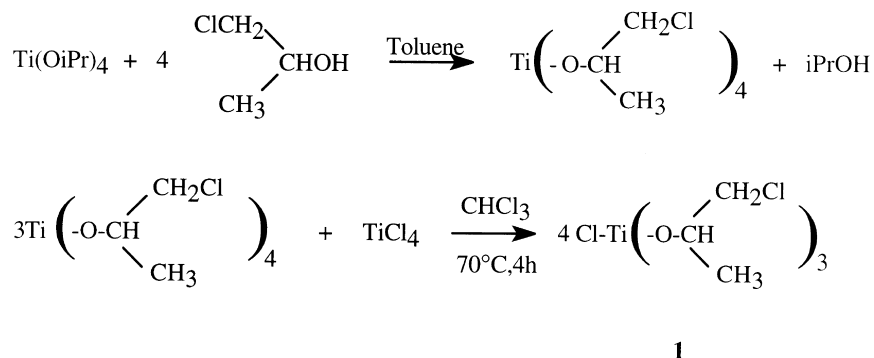
Resin beads prepared by suspension polymerization, if



i) $\text{NH}_2\text{-NH}_2$, Dioxane, 80°C , 2 days; ii) $\text{ClTi}(\text{OCH}(\text{CH}_2\text{Cl})\text{CH}_3)_3$, CHCl_3 , $(\text{Et})_3\text{N}$.

	ACP Resins	HP Resins	TiP Resins
X = 0.10	ACP1	HP1	TiP1
X = 0.27	ACP2	HP2	TiP2
X = 0.40	ACP3	HP3	TiP3
X = 0.50	ACP4	HP4	TiP4

Scheme 1 Preparation of macroporous polymer-supported titanates TiP



1

Scheme 2 Preparation of **1** from $\text{Ti}(\text{OiPr})_4$

suitably crosslinked in the presence of a porogen, form a permanently macroporous structure, hence providing good accessibility to immobilized species¹⁰. Further, whereas soluble polymers bring with them separation problems, spherical polymer resin particulates can improve isolation and purification procedures. Following our previous work on the preparation of poly(*p*-acetoxystyrene) resins¹¹, we prepared, by suspension polymerization, supports ACP1, ACP2, ACP3 and ACP4 bearing different amounts of acetoxy groups for the same nominal crosslinking level (20% mol% of divinylbenzene) using 2-ethylhexanol as precipitating porogen. The characteristics of the different materials obtained are shown in *Table 1*.

Functionalization of beads ACP1 to ACP4 with $\text{ClTi}(\text{OCH}(\text{CH}_2\text{Cl})\text{CH}_3)_3$ **1**

Mixed alkyl titanates have been synthesised in good yields by reaction between an alkoxy titanium halide and another alcohol or phenol in the presence of a base such as pyridine¹². Therefore, we decided to react $\text{ClTi}(\text{OCH}(\text{CH}_2\text{Cl})\text{CH}_3)_3$ **1** with polymer-supported phenol groups directly in the presence of triethylamine. We expected, by this approach, that only the Ti–Cl bond would react, leading to a trichloroisopropyl titanium moiety attached to the support by only one phenoxy group. The principle of the method is shown in *Scheme 1*.

The hydrolysis of the polymer-supported acetoxy group was performed according to a previously described procedure¹³. The corresponding poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) resins HP1–4 were obtained in good yields. The choice of a chlorinated titanium alkoxide as the immobilised species was deliberate to allow the efficiency of the grafting to be estimated by elemental analysis of titanium and chlorine and hence to have an idea of the structure of the species grafted. This immobilisation was performed following two approaches both using an *in situ* preparation of the moiety to be attached.

In a first attempt (Method A), the tri(2-chloroisopropyl) chlorotitanate **1** was prepared from the $\text{Ti}(\text{OiPr})_4$ in a two-step procedure according to *Scheme 2*.

Crude **1** was then condensed, without isolation, with resins HP1 and HP2 in suspension in chloroform in presence of triethylamine to give resins TiP1 and TiP2. The results are reported in *Table 2*.

As there was no direct analysis possible, the phenol group content of HP resins was estimated assuming firstly that acetoxystyrene incorporates onto the copolymer at the initial monomer feed level¹³, and secondly that the hydrolysis of the supported acetoxy groups to give phenol groups is complete (no residual -C=O absorption band in IR after reaction). From the data reported in *Table 2*, it can

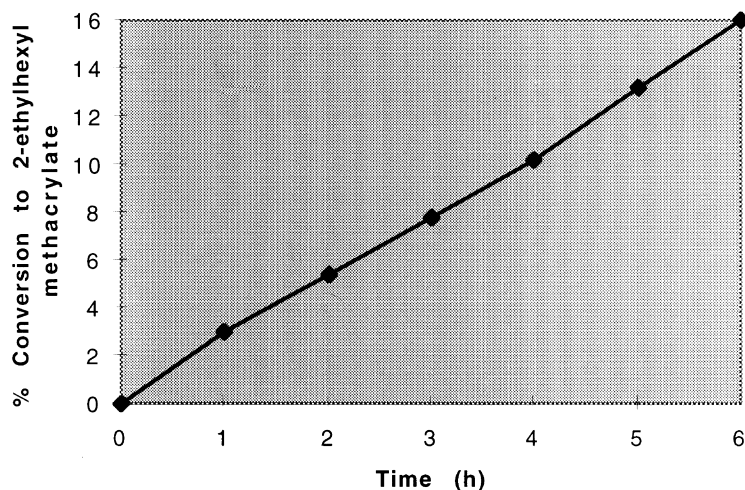


Figure 1 Initial conversion curve for the transesterification of methyl methacrylate with 2-ethylhexanol catalysed by polymer-supported titanate TiP2(II) at 115°C. MMA = 5.6 mol L⁻¹, 2-EH = 2.8 mol L⁻¹, Ti = 0.04 mol L⁻¹, beads = 50 g L⁻¹

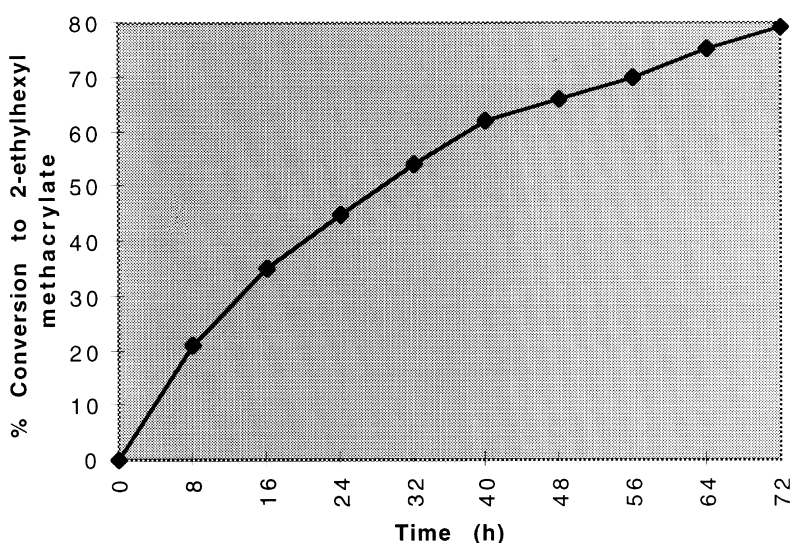
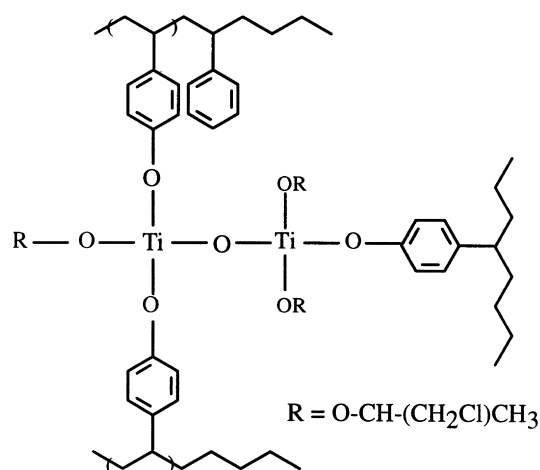


Figure 2 Full conversion curve for the transesterification of methyl methacrylate with 2-ethylhexanol catalysed by polymer-supported titanate TiP2(II) at 115°C. MMA = 5.6 mol L⁻¹, 2-EH = 2.8 mol L⁻¹, Ti = 0.04 mol L⁻¹, beads = 50 g L⁻¹

be concluded that the immobilisation of titanium was achieved in good yield. However the Cl/Ti experimental ratio is low (the expected ratio was 3). This result can be explained by the fact that alkoxy titanium halides derived from reactive alcohols (such as branched or acidic species) tend to decompose upon prolonged heating and disproportionately during distillation¹⁴. In order to test this hypothesis, the chlorine to titanium ratio was estimated in the product of the first step of the synthesis i.e. the Ti(OCH(CH₂Cl)CH₃)₄. The best result obtained for this ratio was 3.6 indicating that a part of the compound had already decomposed.

We therefore tried another approach (Method B). Mikami *et al.*¹⁵ reported that large amounts (5 g/mmol Ti) of activated powdered molecular sieves protect these catalysts from moisture and also facilitate ligand exchange. Commercially available ClTi(OiPr)₃ was therefore mixed with 1-chloropropan-2-ol in the presence of a large amount of molecular sieves. After 4 h at 70°C the mixture was added directly to a suspension of resins HP2, HP3 and HP4 in chloroform in the presence of triethylamine to give TiP2(II), TiP3 and TiP4 resins. The corresponding results are reported in *Table 2*.



Scheme 3 Possible model of structure for the grafted titanates

As can be seen in *Table 2*, no improvement in terms of the Cl/Ti ratio was obtained from this method compared with results depicted from the earlier procedure. Further, the grafting yields tend to be lower. This result suggests that

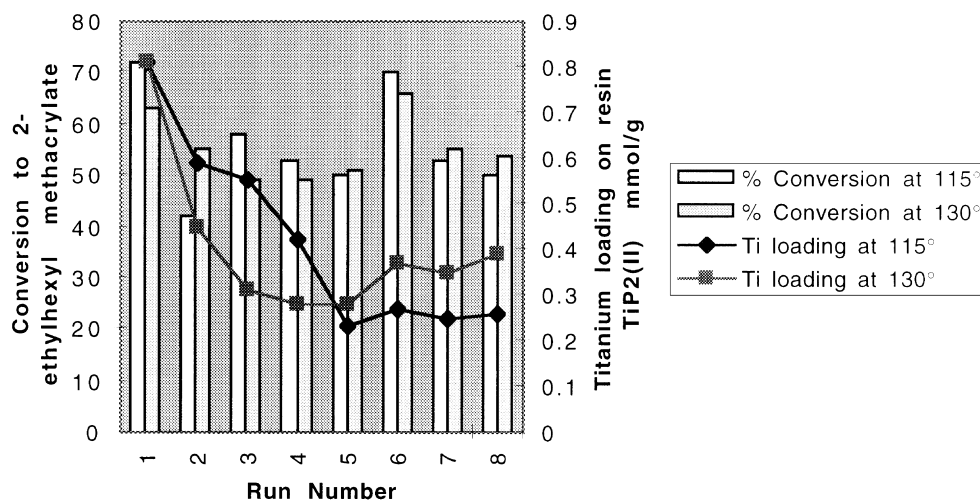


Figure 3 Stability test using resin TiP2(II) as catalyst in the transesterification of methyl methacrylate with 2-ethylhexanol at 115°C and 130°C. MMA = 5.6 mol L⁻¹, 2-EH = 2.8 mol L⁻¹, Ti = 0.04 mol L⁻¹, beads = 50 g L⁻¹

there is no 'site isolation' on the resins. This fact combined with a lack of chemo-selectivity in the breaking of the Ti-Cl bond relative to the Ti-O bond under the conditions used implies secondary crosslinking of the resin by the titanates, with each Ti centre being covalently attached either to the backbone by more than one bond or to several other titanates. For example the representative structure drawn in *Scheme 3* would have a Cl/Ti molar ratio of 1.5 and an apparent loading of Ti of 66%.

This assumption is confirmed by the fact that the higher the hydroxyl group content in the polymer, the lower the ratio of chlorine to titanium. Conversely, higher apparent grafting yields of Ti were reached with lower phenol loading (*Table 2*, sample TiP2) as a result of oligomerisation of the titanate. In spite of these apparently disappointing results we decided to test the polymer-supported titanates obtained as a catalyst for transesterification reactions.

Transesterification tests

Transesterification of methyl methacrylate with 2-ethylhexanol. Transesterification of methyl methacrylate (MMA) with a high boiling point alcohol is a reaction of industrial interest¹⁶. We chose the preparation of one of the most important higher alkyl methacrylic acid esters, the 2-ethylhexyl ester (2-EHMA), as a model reaction for the testing of our supported catalysts.

Kinetic studies were performed at 115°C in neat 2-ethylhexanol (2-EH) with a two-fold excess of methyl methacrylate, using 1.5 mol% Ti as catalyst (TiP2(II)). The formation of the 2-ethylhexyl methacrylate was followed by GC analysis. The resulting kinetic curve at low conversion of 2-ethylhexanol is reported in *Figure 1*.

The conversion of 2-ethylhexanol is a linear function of time up to 16% (over 6 h reaction time). The rate law, $r = k[2\text{-EH}][\text{MMA}][\text{CAT}]$ previously established for an alkoxy titanate supported on silica⁸, seems to apply in our system as well, though of course a more detailed kinetic study is required to confirm this.

From *Figure 1*, the initial experimental rate r for the transesterification of methyl methacrylate with 2-ethylhexanol catalysed with resin TiP2(II) is $r = 30 \times 10^{-6} \text{ L}^{-1} \text{ mol s}^{-1}$. Considering the initial conditions used, the experimental rate constant $k = 5.7 \times 10^{-5} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ can be estimated. Under the same conditions the value for soluble Ti(OiPr)₄ is

$k = 193 \times 10^{-5} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. These data are of the same order of magnitude as those reported for the transesterification of methyl methacrylate with 1-dodecanol using a silica-supported titanate¹⁷. (*Note:* This estimation is based on [CAT] being calculated from Ti moles contained in the total reaction volume and so has no real significance. It does, however, allow a superficial comparison with the homogeneous system and the published silica-supported system¹⁷).

The maximum conversion to 2-ethylhexyl methacrylate reached under the same conditions is reported in *Figure 2*.

Recycling tests

Resin TiP2(II) was used in recycling tests employing the same model reaction. The supported catalyst was filtered and dried between each reuse. Each run was stopped after 24 h and the ester formed was purified via silica gel column chromatography. The results of the recycling are reported in *Figure 3*.

The yield of isolated 2-ethylhexyl methacrylate lies consistently between 50 and 70%. Within experimental error, the 24 h conversion is quite steady even after 8 recycles, and despite operating at 115°C or 130°C, the polystyrene-based catalyst shows remarkable stability. There is little difference in terms of stability and rate between the reactions performed at 115°C and 130°C. The apparently high level of leaching of Ti (more than 50%) seems to be incompatible with the consistency of the conversion over 24 h observed during the successive reuse of the same catalyst sample. A possible explanation is that unreacted vinylic bonds in the resin undergo copolymerization with methyl methacrylate during the reaction, leading to an apparent weight increase of the support. In order to check this point, we decided to study the transesterification of a non-polymerisable ester.

Transesterification of ethyl butyrate with dodecanol

The catalytic activity of resin TiP2(II) was tested in the transesterification of ethyl butyrate (EB) with dodecanol (D) at 115°C. The recycling capability and the leaching of titanium were probed in several reuses of the same resin in successive batches with a simple washing between batches. The results are reported in *Figure 4*.

The conversion to dodecyl butyrate as estimated by GC is low but constant during the successive runs. More

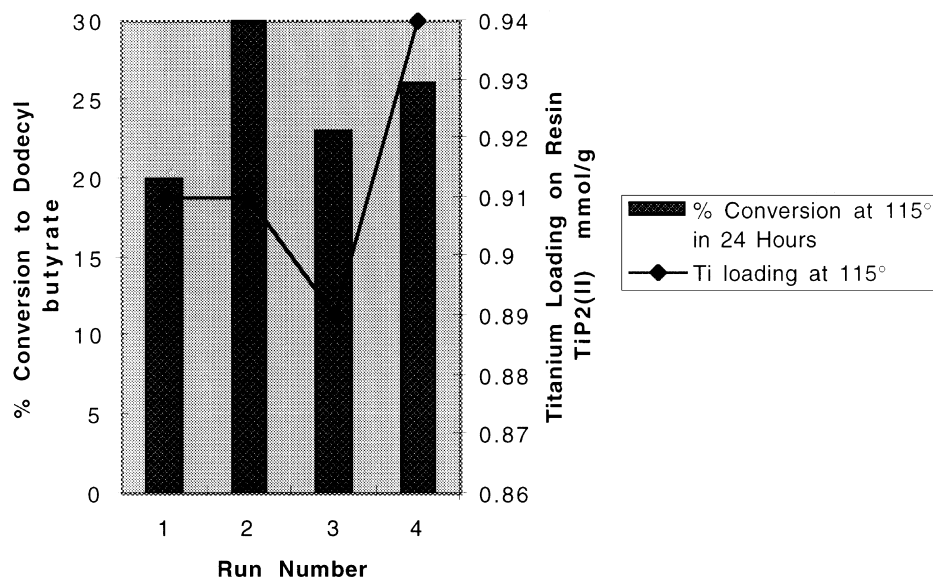


Figure 4 Stability and titanium leaching for the resin TiP2(II) as catalyst during recycling in the transesterification of ethyl butyrate with dodecanol at 115°C. EB = 2.8 mol L⁻¹, D = 2.8 mol L⁻¹, Ti = 0.04 mol L⁻¹, beads = 50 g L⁻¹

interesting is the relatively high stability of the catalyst as indicated by only small changes in the Ti content which probably reflects simply the error in the estimation. This observation suggests that the fall in Ti content (mmol g⁻¹) of the catalyst in the methyl methacrylate reaction is an artefact, arising from an increase in mass of the resin from grafted methacrylate polymer. The results also seem to indicate that the reaction involves the Lewis-acid properties of the Ti centre rather than a ligand exchange which would contribute to loss of Ti and therefore loss of activity.

CONCLUSION

The tri(2-chloroisopropoxy)titanium moiety has been covalently attached to a macroporous polymeric support by functionalisation of a poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) resin with the corresponding chlorotrialkyltitanate. The presence of a chlorine atom on the alkyl moiety allows some idea to be obtained of the real structure of the grafted species. The low molar ratio Cl/Ti (< 1) obtained shows that the alkyl titanates form a secondary crosslink. The resulting polymer-supported titanates have been tested as catalysts in the transesterification of methyl methacrylate with a high boiling point alcohol, 2-ethylhexanol. The relatively high initial reaction rate measured, as well as the great stability of the catalyst during successive cycles, make these catalysts a viable alternative to the more toxic dibutyltin oxide commonly used. Similar recycling tests using a non-polymerisable ester allowed us to show a low leaching of titanium during successive runs.

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