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Silica-Supported Zirconium Complexes and their Polyoligosilsesquioxane Analogues in the Transesterification of Acrylates: Part 2. Activity, Recycling and Regeneration

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Abstract: The catalytic activity of both supported and soluble molecular zirconium complexes was studied in the transesterification reaction of ethyl acrylate by butanol. Two series of catalysts were employed: three well defined silica-supported acetylacetonate and *n*-butoxy zirconium(IV) complexes linked to the surface by one or three siloxane bonds, $(\equiv SiO)Zr(acac)_3$ (**1**) $(\equiv SiO)_3Zr(acac)$ (**2**) and $(\equiv SiO)_3Zr(O\text{-}n\text{-}Bu)$ (**3**), and their soluble polyoligosilsesquioxy analogues $(c\text{-}C_5H_9)_7Si_8O_{12}(CH_3)_2Zr(acac)_3$ (**1′**), $(c\text{-}C_5H_9)_7Si_7O_{12}Zr(acac)$ (**2′**), and $(c\text{-}C_5H_9)_7Si_7O_{12}Zr(O\text{-}n\text{-}Bu)$ (**3′**). The reactivity of these complexes were compared to relevant molecular catalysts [zirconium tetraacetylacetonate, $Zr(acac)_4$ and zirconium tetra-*n*-butoxide, $Zr(O\text{-}n\text{-}Bu)_4$]. Strong activity relationships between the silica-supported complexes and their polyoligosilsesquioxane analogues were established. Acetylacetonate complexes were found to be far superior to alkoxide complexes. The monopodal complexes **1** and **1′** were found to be the most active in their respective series. Studies on the recycling of the heterogeneous catalysts showed significant degradation of activity for the acetylacetonate complexes (**1** and **2**) but not for the less active tripodal alkoxide catalyst, **3**. Two factors are thought to contribute to the deactivation of catalyst: the lixivation of zirconium by cleavage of surface siloxide bonds and exchange reactions between acetylacetonate ligands and alcohols in the substrate/product solution. It was shown that the addition of acetylacetone to the low activity catalyst $Zr(O\text{-}n\text{-}Bu)_4$ produced a system that was as active as $Zr(acac)_4$. The applicability of ligand addition to heterogeneous systems was then studied. The addition of acetylacetone to the low activity solid catalyst **3** produced a highly active catalyst and the addition of a stoichiometric quantity of acetylacetone at each successive batch catalytic run greatly reduced catalyst deactivation for the highly active catalyst **1**.

Keywords: acetylacetonate and alkoxy ligands exchange; catalyst regeneration; recycling; silica-supported zirconium complexes; transesterification of (meth)acrylates

Introduction

Transesterification reactions represent one of the classic reactions in organic chemistry. They are of great practical industrial interest because they are often realized under mild conditions and thus can be a convenient means to prepare esters not accessible by direct esterification reactions.[1] Transesterification products are used not only in organic synthesis but also in polymerization reactions and can find large applications in industry particularly in the coatings industry. The acid-[2] and base[3]-catalyzed transesterification reactions were largely investigated during the 1950s and 1960s. They are now replaced by metal catalysts (Al, Pb, Sn, etc.)[4] and particularly transition metal catalysts (Ti, Zr, etc.)[5] which render the transesterification more chemo-, stereo- and regioselective. These latter suffer, nevertheless, from the problems of homogeneous catalysis concerning the recovery of the catalyst from the reaction mixture at the end of the reaction and eventually its recycling. The development of selective, ecofriendly and reusable solid catalyst for organic transformations is a very active research area and in the particular case of transesterification reactions a large variety of heterogeneous catalysts has been reported so far including Brønsted acid solids,[6] organic nitrogen bases-modified mesoporous silica materials[7] and titanates immobilized on different supports such as alumina, silica and polymers.

The high activity and selectivity of titanates as homogeneous catalysts in the transesterifications of acrylic esters which are useful substrates for a variety of synthetic transformations[5] has prompted considerable effort to find efficient immobilization strategies not only from an environmental and economical point of view but also to favour the formation on the solid surface of monomeric titanium species thought to be the true active catalytic centers. Supported transesterification titanium alkoxides-based catalysts were synthesized by Blandy and co-workers[8] by reacting $XTi(OR)_3$ ($X=CH_3$, Cl, O-*i*-Pr) with alumina and silica surfaces. These catalysts were able to catalyze the transformation of ethyl propionate by 1-dodecanol to produce 1-dodecyl propionate. Although recycling of the solid catalysts was reported, the activity was lower than that of the homogeneous analogues. Besides, alkyltitanates covalently attached to macroporous poly(4-hydroxystyrene-co-divinylbenzene) resins were also found to promote the transesterification of methyl methacrylate (MMA) with 2-ethylhexanol or 1-dodecanol but here again moderate activity was achieved.[9a] An improvement of the activity was obtained by anchoring alkoxytitanates, $Ti(O\text{-}i\text{-}Pr)_4$, on resins with increasing levels of cross-linking.[9b] However, the rate of the transesterification decreased slowly upon recycling due to some plugging of the pores by poly(methacrylate). Recently, in order to improve the stability of the SiO–Ti bond in silica-grafted titanium catalysts a passivation step was introduced in the catalyst synthesis protocol by reacting the residual silanol groups with 1-(trimethylsilyl)imidazole. This synthetic route did not lead to any further improvement since titanium leaching was always detected in the heterogeneous transesterification of methyl methacrylate with butanol in the liquid phase.[10]

At the industrial level, Rohm and Haas has described, in two patents,[11] the preparation of titanium and zirconium alkoxides or acetylacetonate catalysts supported on organic or inorganic supports and having a polymerizable function which can be polymerized before or after the grafting. These catalysts were reported as being able to transesterify an important number of esters among them acrylates, not always easy to transform, under mild conditions.

Thus, although attempts to recycle heterogeneous titanates have been reported, a loss of activity due to the leaching of the metal in solution was often observed. This is not surprising since titanium-based catalysts are known to be sensitive towards hydrolysis and alcoholysis. Note that in the case of transesterification reaction this lack of stability represents a significant limitation since the alcohol is used both as reactant and solvent. On the other hand, it was determined that zirconium(IV) acetylacetonate complexes such as $Zr(acac)_4$, whether homogeneous or heterogeneous, were highly efficient and selective catalysts for the transesterification of (meth)acrylates and more stable than their titanate counterparts upon recycling.[9b]

With this in mind, our initial objective in this study was thus to produce an active supported analogue of the homogeneous $Zr(acac)_4$ using a silica carrier, which would simplify the overall process. This was accomplished *via* surface organometallic chemistry by extending established work from our laboratory on supported zirconium complexes.[12] We have described in part 1 of this series of publications[13] the synthesis and the characterization of three relatively well defined silica-supported acetylacetonate and butoxy zirconium(IV) complexes linked to the surface by one or three siloxane bonds, $(\equiv SiO)Zr(acac)_3$ (**1**), $(\equiv SiO)_3Zr(acac)$ (**2**), and $(\equiv SiO)_3Zr(O\text{-}n\text{-}Bu)$ (**3**) as well as the synthesis of their soluble polyoligosilsesquioxy analogues $(c\text{-}C_5H_9)_7Si_8O_{12}(CH_3)_2Zr(acac)_3$ (**1′**), $(c\text{-}C_5H_9)_7Si_7O_{12}Zr(acac)$ (**2′**), and $(c\text{-}C_5H_9)_7Si_7O_{12}Zr(O\text{-}n\text{-}Bu)$ (**3′**) (Figure 1). We wish now to examine the catalytic behaviour of these supported and molecular complexes in the transesterification of acrylates, the recycling of the surface species, easier to recover after the catalysis than their soluble analogues, and explore the question of catalyst ageing and regeneration.

Results and Discussion

Choice of Catalytic Testing Conditions

With the objective of developing a general use heterogeneous transesterification catalyst and studying its behaviour under laboratory and micropilot reaction conditions, one must choose a relevant model system and reaction protocol capable of producing and reproducing measurable results. The approach taken in this study was to choose a simple general homogeneous catalyst [$Zr(acac)_4$] and a model reaction (see below), and then proceed through a series of experimental and analytical protocols to determine which would most simply provide an adequate measure of activity. With regards to the catalytic reaction, we chose to study the transformation of ethyl acrylate (AE) by *n*-butanol to give *n*-butyl acrylate (ABu) and ethanol (Scheme 1). As was mentioned in the introduction, (meth)acrylates are useful synthons for the synthesis of relevant fine chemicals, polymers and important intermediates for oil and coatings industry, as evidenced

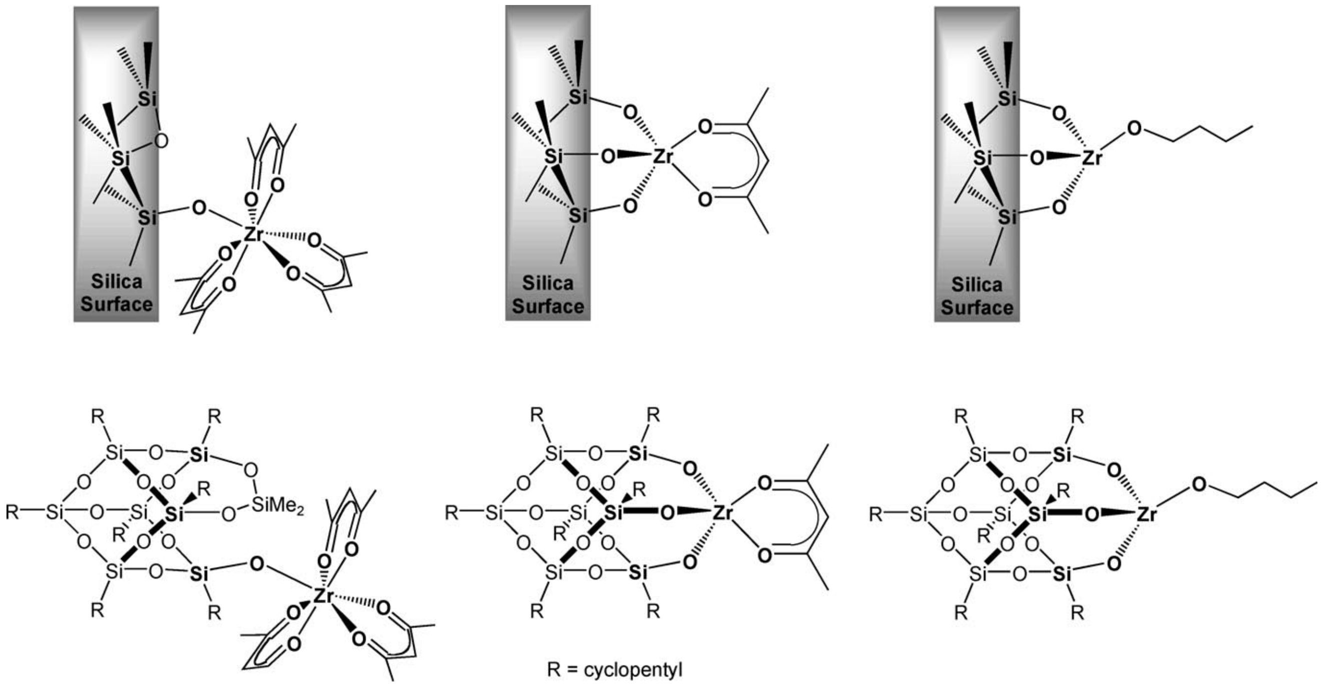
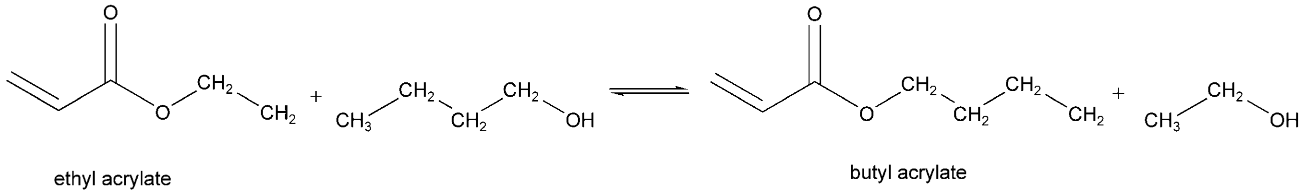


Figure 1. Monopodal and tripodal acetylacetonate and butoxy zirconium surface complexes and their soluble polysilsesquioxane models.



Scheme 1.

by the significant number of mentions in the patent literature.[14]

Several options were considered with respect to the reaction protocol.[15] In our case, we chose to work in a batch reactor and evaluate the activity in terms of the kinetic approach to the reaction equilibrium. Catalysis was therefore realized very simply in a two-necked flask under argon at atmospheric pressure, at 70 °C, without any solvent, with an equimolar mixture of ethyl acrylate and *n*-butanol and a molar ratio *n*-BuOH/Zr of 1000.

The advancement of each test is represented by plot of "extent of reaction" *versus* time. Extent of reaction, α, is defined as the percentage of *n*-BuOH converted to *n*-butyl acrylate divided by the equilibrium constant at the temperature of the reaction (0.51 at 70 °C) [Eq. (1)] and is expressed as a percentage. Thus, the plot begins at $\alpha = 0$ and if equilibrium is obtained, the curve levels off at $\alpha = 100\%$. In tabular form, activity is expressed as initial rate of butyl acrylate formation (determined graphically, expressed as $\mathrm{mM\,min^{-1}}$) and as the extent of the reaction at 6 h (or, if equilibrium is reached more quickly, we note the time at which the extent of reaction passes 95%). The selectivity of the reaction, that is the number of moles of butyl acrylate formed divided by the number of moles of *n*-BuOH which had reacted, was found to be unity within experimental error in all cases reported in this paper.[16]

$$\alpha = [\text{butyl acrylate}]_t/[\text{BuOH}]_0 \text{Keq} \qquad (1)$$

Evaluation of the Catalytic Activity of the Surface Species and of their Molecular Analogues

Recall that, in Part 1 of this series of reports,[13] a series of silica-supported zirconium acetylacetonate and alkoxide complexes and their polyoligosilsesquioxane analogues were synthesized and fully characterized by a series of spectroscopic and chemical techniques. These complexes were submitted to the standard catalytic reaction protocol described above, together with the homogeneous benchmark catalysts,

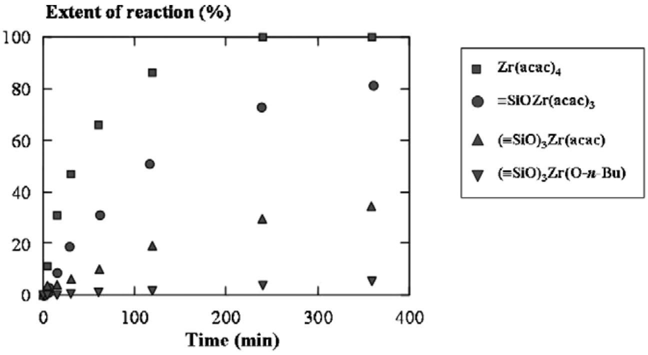


Figure 2. Catalytic activity of the surface species **1**, **2** and **3** in the transesterification of ethyl acrylate by *n*-butanol.

zirconium tetraacetylacetonate, $Zr(acac)_4$, and zirconium tetra-*n*-butoxide, $Zr(O\text{-}n\text{-}Bu)_4$.

Before testing the reactivity of the surface zirconium species, a blank run was performed on the silica support, previously dehydroxylated at 500 °C. Under the standard conditions, no *n*-butyl acrylate product was observed after six hours of reaction in the reaction medium. Thus, the support exhibits no measurable activity toward transesterification.

A first series of tests was performed comparing three heterogeneous catalysts, the monopodal tris-acetylacetonate complex **1**, the tripodal mono-acetylacetonate complex, **2**, and the tripodal monobutoxide complex **3**, to the homogeneous analogue, $Zr(acac)_4$, (Figure 2).[17] The supported catalysts had similar zirconium loadings (2.64–2.68%$_{wt}$ Zr). Note especially that in this series of experiments, the *number of moles of zirconium* introduced into the reactor was held constant.

The three heterogeneous catalysts all exhibit catalytic activity, although inferior to the activity of the homogeneous $Zr(acac)_4$ catalyst. The best of the heterogeneous catalysts, the monopodal tris-acetylacetonate complex **1**, was only half as active as $Zr(acac)_4$ (60 mM min^{-1} *vs.* 26 mM min^{-1}, Table 1). Furthermore, the ligand systems have a strong effect on catalytic activity. The tripodal acetylacetonate complex **2** was far less active (8.6 mM min^{-1}), and the monopodal alkoxide complex **3** was nearly inactive (0.65 mM min^{-1}). This result is not pre-ordained, as one can note that for titanium homogeneous catalysts the alkoxides are among the most active catalysts for transesterification and esterification reactions but that was not the case here.

Table 1. Transesterification of ethyl acrylate by *n*-butanol catalyzed by silica-supported and molecular zirconium complexes.

Catalyst	Zr loading for solid catalyst [%$_{wt}$]	α at 6 h	Initial rate [mM min^{-1}]
$Zr(acac)_4$	Homogeneous	(eq. at 175 min)	60
1	2.64	85	26
2	2.68	33	8.6
3	2.67	6	0.65
1′	Homogeneous	92	52
2′	Homogeneous	27	2.2
3′	Homogeneous	5	0.65
$Zr(O\text{-}n\text{-}Bu)_4$	Homogeneous	5	0.80

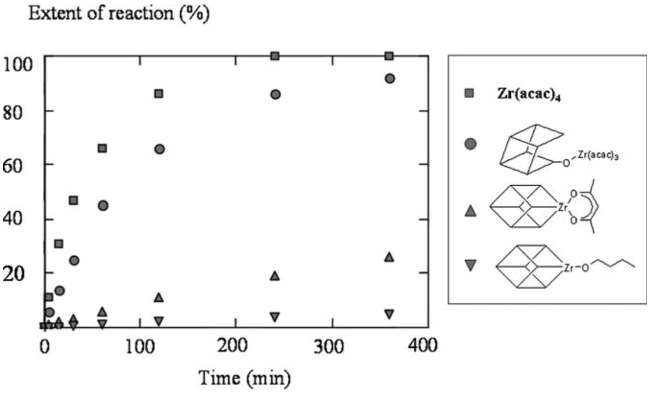


Figure 3. Catalytic activity of the soluble analogues **1′**, **2′** and **3′** in the transesterification of ethyl acrylate by *n*-butanol.

This catalytic activity trend was mirrored for the molecular catalysts **1′**, **2′**, and **3′** (Table 1, Figure 3). The monopodal silsesquioxane catalyst **1′** was twice as active as its heterogeneous analogue **1**, (52 mM min^{-1} *vs.* 26 mM min^{-1}), indeed nearly as active as $Zr(acac)_4$ (52 mM min^{-1} *vs.* 60 mM min^{-1}). The initial activity of the tripodal acetylacetonate complex, **2′** drops to 2.2 mM min^{-1}, and again the alkoxide catalyst **3′** was nearly inactive (0.65 mM min^{-1}).

Thus, one observes, in terms of initial catalytic activity, that acetylacetonate complexes are superior to alkoxide complexes in this series, and that structure-activity trends exhibited by the supported complexes are mirrored for the molecular analogues.

Recycling of the Surface Zirconium Species 1, 2 and 3

We considered that catalyst stability and regeneration were of primal interest. Thus, a preliminary study of the performance of each heterogeneous catalyst over several batch reaction cycles was investigated. The protocol was as follows. Fresh catalyst was employed under the conditions detailed above and allowed to react for six hours. The catalyst was then allowed to settle overnight and the solution was withdrawn *via* syringe. Fresh substrate solution was then added and the reactor was again heated to 70 °C. After six hours of reaction, the same recycling/reaction protocol was repeated, thus producing three successive six-hour catalytic runs (performed over three days) for each catalyst.

The results for monopodal surface catalyst **1** are shown in Figure 4. One observes a sharp decrease in activity. In terms of initial activity, the second cycle was 3.5 times less active than the fresh catalyst (*cycle 1*, 26 mM min^{-1}; *cycle 2*, 7.5 mM min^{-1}) and the third cycle further deactivated by a factor of three (*cycle 3*, 2.5 mM min^{-1}, an overall activity loss of 90% from the initial run).

One might envisage that this drop in activity could be due to lixivation. To investigate this hypothesis, a number of different methods were employed. The zirconium microanalysis of used catalyst at the end of the third catalytic run (after two recyclings) showed that approximately 25% of the grafted zirconium had been lost (1.92%$_{wt}$ Zr *vs.* 2.64%$_{wt}$ Zr). Otherwise stated, during the third run, more than 75% of the grafted zirconium is present but catalytic activity has dropped off by 90%. This suggests that lixivation cannot be the sole cause for catalyst deactivation.[18]

Given that the catalyst is in powdered form, one might postulate also that some finely divided catalyst is lost at the decantation step of the recycling protocol, that is, a finely divided powder was suspended in the supernatant. As a control, a catalyst analogous to **1** was prepared using high specific surface (380 m^2·g^{-1}) silica beads. The activity of this catalyst mirrored, at a very slightly inferior activity level, that of **1** over three cycles.

Acetylacetone was detected (but not quantified)[19] in solution after each catalytic run. This observation lead to a study of ligand exchange as a possible origin of the sharp catalytic activity losses observed, below.

Similar recycling behaviour was observed for the tripodal monoacetylacetonate complex **2** (Figure 5). Initial activity dropped sharply from 8.6 mM min^{-1} for fresh **2** to 3.2 mM min^{-1} for the second cycle (63% activity loss) and 0.65 mM min^{-1} for the third cycle (92% overall activity loss). In this case, however, zirconium microanalysis of used catalyst showed no difference with that of fresh catalyst. Significantly, acetylacetone was once again detected (but not quantified)[19] in the solution.

Finally, the relatively inactive tripodal butoxide zirconium catalyst **3** was submitted to the recycling protocol (Figure 6). This relatively poor catalyst exhibited no significant activity loss over the three cycles (initial activity for each cycle was 0.65 mM min^{-1}). As shall be seen below, the fact that the initial activity of the tripodal alkoxide catalyst **3** and that of the used tripodal acetylacetonate catalyst **2** were identical may not be accidental. One should also note that zirconium microanalysis showed no significant change between fresh catalyst and used catalyst.

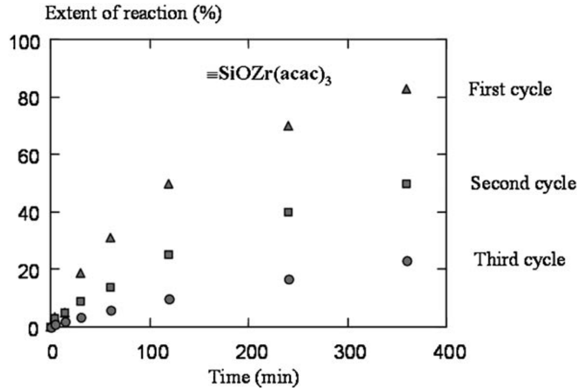


Figure 4. Recycling of (≡SiO)Zr(acac)$_3$ (**1**).

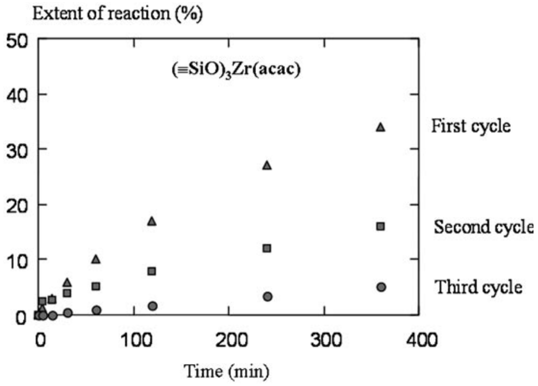


Figure 5. Recycling of (≡SiO)$_3$Zr(acac) (**2**).

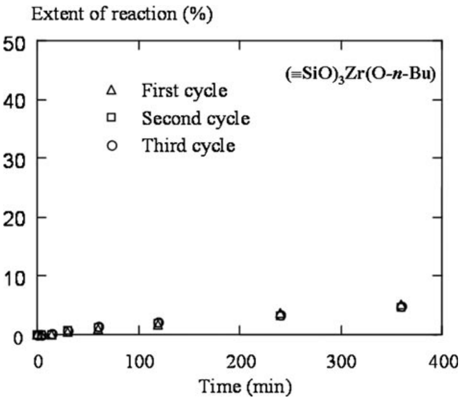


Figure 6. Recycling of (≡SiO)$_3$ZrO-*n*-Bu (**3**).

Regeneration of Catalytic Activity

Given that the loss of activity of supported acetylacetonate complexes was accompanied by the presence of acetylacetone in the product solution and that the tripodal butoxide zirconium complex did not lose activity on recycling, it seemed clear that part of deactivation could be due to the replacement of acetylacetonate ligands by butoxide ligands. The exchange be-

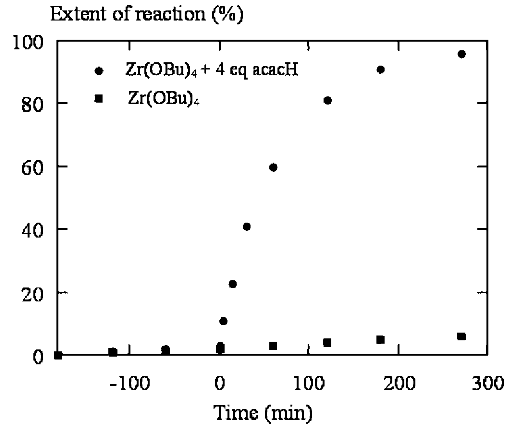


Figure 7. Transesterification of ethyl acrylate by butanol catalyzed by Zr(O-*n*-Bu)$_4$ with and without added acetylacetone after 3 h.

tween alkoxide ligands and β-diketone chelating ligands at zirconium and titanium has been thoroughly studied[20] and it has been established that the exchange is facile, that mixed alcoholate/chelate complexes are often stable and less susceptible to hydrolytic degradation than the simple alkoxides.[21] The formation of zirconium alkoxides from acetylacetonate complexes seemed likely due to the high concentration of butanol (initially one thousand times that of the zirconium) and a reaction temperature (70 °C) sufficient to facilitate ligand dissociation. Furthermore, we recognized that we might be able to regenerate the deactivated catalysts by addition of acetylacetone.

The hypothesis was first explored in a homogeneous system, using the inactive tetrabutoxyzirconium, Zr(O-*n*-Bu)$_4$, as the catalyst. Recall that the activity of this catalyst is very close to that shown by **3** and **3′** (Table 1). In Figure 7, we have represented two experiments – in the first one, following the standard catalytic protocol, the mixture of butanol and ethyl acrylate were allowed to react in the presence of Zr(O-*n*-Bu)$_4$ at 70 °C for six hours, resulting in a low initial rate of reaction (0.8 mM min^{-1}), which does not vary significantly given the very low conversions. In a second experiment, an identical protocol was followed for the first three hours of reaction, at which point four equivalents of acetylacetone were introduced. The catalytic activity of the reaction immediately increases to a level of the same order as that of Zr(acac)$_4$ catalyst: if one measures "initial activity" from the point where the acetylacetone was added, one observes 23 mM min^{-1}, which can be compared to the 60 mM min^{-1} observed for Zr(acac)$_4$. Clearly, one can regenerate at least partially catalytically active species from inactive catalysts in this manner.

This protocol was used to determine the optimal ligand to zirconium ratio. That is, in each experiment the standard protocol was followed for three hours with Zr(O-*n*-Bu)$_4$, at which point different quantities of acetylacetone were added to the reactor (Figure 8). Important increases in activity were observed in all cases, even when less than one equivalent of acacH was employed. The best activity was obtained by the addition of three equivalents of acetylacetone (60 mM min^{-1}), equivalent to that observed for Zr(acac)$_4$. Higher concentrations of acetylacetone appear to inhibit catalytic activity (Figure 9). One might suppose that the catalysis involves coordination of substrate to zirconium, and that excess acetylacetone competes favourably with substrate for coordination. It would follow that the most active species

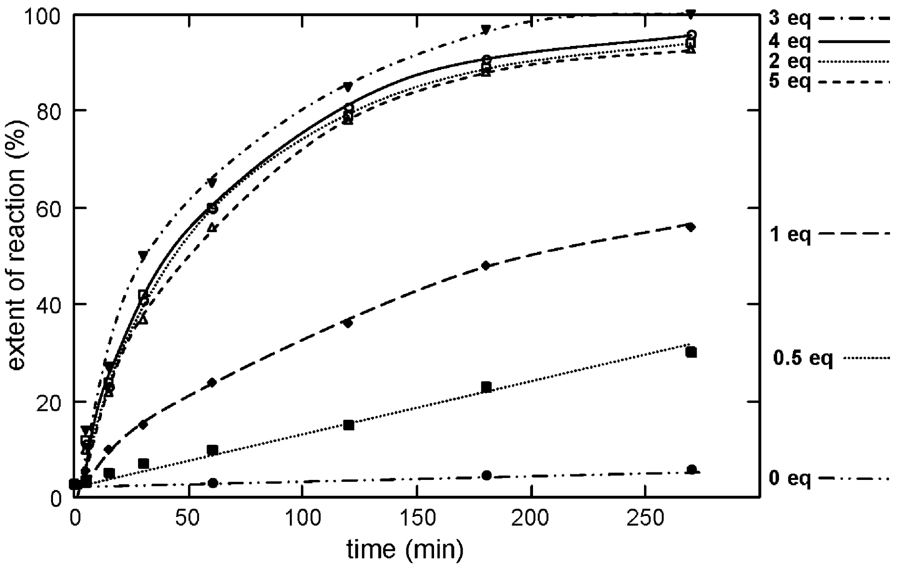


Figure 8. Influence of the quantity of added acetylacetone on the transesterification reaction catalyzed by Zr(O-*n*-Bu)$_4$.

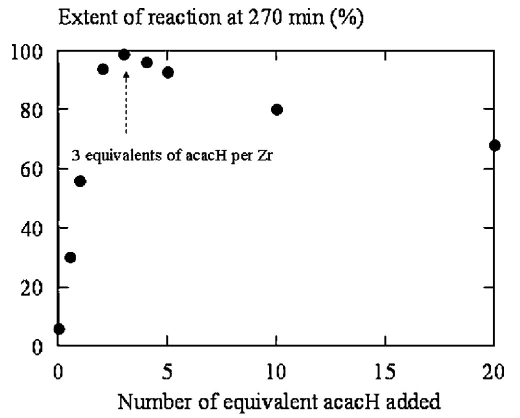


Figure 9. Influence of the quantity of added acetylacetone on the transesterification reaction catalyzed by $Zr(O\text{-}n\text{-}Bu)_4$ at 270 min.

would be a trisacetylacetonate species, but verification of this hypothesis has not been pursued.

Ligands Exchange in Heterogeneous Catalysis

Recall that the overall objective of this project was the development of more active and stable heterogeneous catalysts for industrial application. Given the ligand exchange hypothesis, and in the context of multicycle industrial application, we consider that the two tripodal catalysts, **2** and **3**, are functionally equivalent and thus we have two types of systems, monopodal and tripodal. Thus, the *in situ* generation of an active catalyst from an inactive catalyst was attempted by adding acetylacetone (6 equivalents) to a test of the tripodal butoxide catalyst, **3** (Figure 10). The resultant system exhibited an activity similar to that of the tripodal zirconium acetylacetonate material **2**.

As a preliminary step to our studies on the use of ligand addition to maintain activity under industrial micropilot conditions,[22] a study was performed in order to check if the addition of acetylacetone to the batch reactor feed would have an effect on catalyst stability. The monopodal trisacetylacetonate zirconium catalyst **1**, which exhibited the highest activity but deactivated very quickly, was chosen for this study. Fresh catalyst was employed as usual for the recycling series of experiments, that is, reacted with the substrate mixture at 70 °C for six hours, left to stand at room temperature overnight, and separated by decantation. In the second and third cycles, a stoichiometric quantity of acetylacetone (1 equivalent per zirconium, 11 mg) was added to the substrate mixture (acacH is thus ~$0.04\%_{wt}$ of the reactor feed). As can be seen in Figure 11, very little change in activity was observed for the first recycled run (indeed, it is slightly more active), and in subsequent runs the activity losses are far less significant than those observed when pure substrate is employed (see Figure 4). It may be that this loss of activity is due to lixivation, given the evidence for this process mentioned above (see also ref.[18]). Nevertheless, the study provides very encouraging indications as to the direction to follow in the development of stable and robust heterogeneous transesterification catalysts.

Conclusions

In this study, a series of homogeneous and heterogeneous zirconium catalysts was evaluated for the transesterification of ethyl acrylate by butanol under varying catalytic protocols. It was shown that the relationship between the structure of the catalyst and its activity and stability for silica-supported zirconium complexes was mirrored by their polyoligosilsequioxane

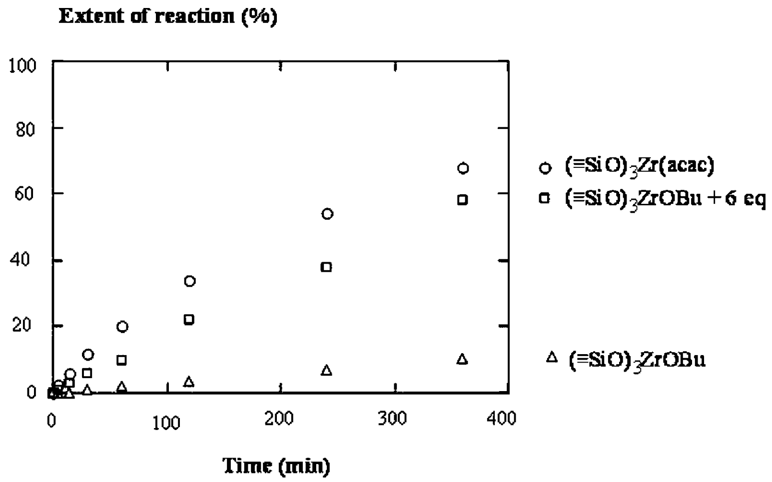


Figure 10. Effect of added acetylacetone on the transesterification reaction catalyzed by $(\equiv SiO)_3Zr(O\text{-}n\text{-}Bu)$ (**3**).

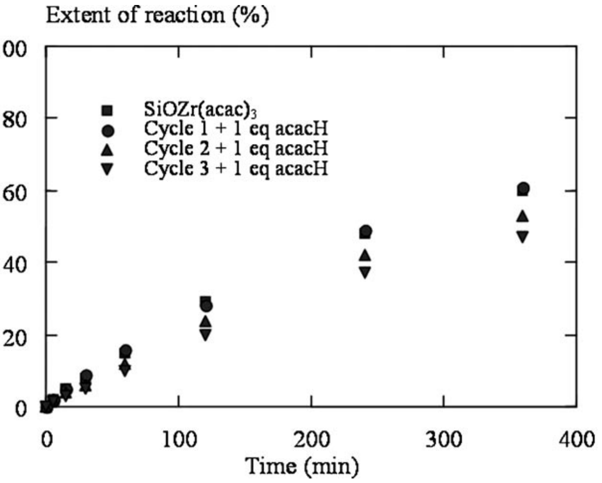


Figure 11. Attempt to regenerate monopodal surface species $(\equiv SiO)Zr(acac)_3$ (**1**) by addition of 1 equiv. of acetylacetone.

analogues. Acetylacetonate complexes were found to be far superior to alkoxide complexes. Little difference in terms of absolute initial activity was observed between the heterogeneous catalysts (**1**, **2** and **3**) and homogenous catalysts (**1′**, **2′** and **3′**). The monopodal complexes **1** and **1′** were found to be the most active in their respective series. Studies on the recycling of the heterogeneous catalysts showed significant degradation of activity for the acetylacetonate complexes (**1**, **2**) but not for the less active tripodal alkoxide catalyst **3**. Two main factors contribute to the deactivation of catalyst. The lixivation of zirconium by cleavage of surface siloxide bonds, presumably by alcohol, was observed with the monopodal catalyst **1**, but to no significant extent for **2** and **3**. Ligand exchange reactions between alcohols in the substrate/product solution and the catalyst leading progressively to the less active alkoxide analogues was also invoked and further studied. The facility of ligand exchange under catalytic conditions was demonstrated: the low activity homogeneous catalyst $Zr(O\text{-}n\text{-}Bu)_4$ was rendered much more active by the addition of actetylacetone. The addition of an optimal amount of acetylacetone (3 equivalents) produced a system that was as active as $Zr(acac)_4$. The applicability of ligand addition to heterogeneous systems was then studied. The addition of six equivalents of acetylacetone to the low activity solid catalyst **3** was shown to produce a highly active catalyst. Initial studies on producing steady catalytic activity were invoked, and it was shown that the addition of a stoichiometric quantity of acetylacetone ($0.04\%_{wt}$ with respect to zirconium) to each portion of the batch catalytic reactor feed greatly reduced catalyst deactivation of the highly active, easily degraded catalyst **1**.

Future publications in this series will concentrate on ligand effects on the reaction, on the role of the silica surface in catalyst degradation and on industrial micropilot studies of the transesterification reaction.

Experimental Section

All manipulations, when needed, were conducted under strict inert atmosphere or vacuum conditions using Schlenk techniques. The solvents were dried using standard methods and stored over activated 4 Å molecular sieves. $Zr(acac)_4$ and $Zr(O\text{-}n\text{-}Bu)_4$ in solution in *n*-butanol were purchased from Aldrich Chemical and used without further purification. Ethyl acrylate was provided by Elf-Atochem. Before reaction with molecular zirconium complexes, silica (Aerosil from Degussa, $200\ m^2 g^{-1}$) was first calcined at 500 °C under a stream of O_2 for 15 h followed by dehydroxylation under vacuum (10^{-5} mm Hg) at the same temperature. Three silica-supported acetylacetonate and butoxy Zr(IV) complexes with different coordination spheres and links with the silica support have been prepared and fully characterized in Part 1 of this series of papers (for more details see ref.[13]). $(\equiv SiO)Zr(acac)_3$ (acac = acetylacetonate ligand) (**1**) was obtained by direct reaction of $Zr(acac)_4$ with $silica_{(500)}$ whereas $(\equiv SiO)_3Zr(acac)$ (**2**) and $(\equiv SiO)_3Zr(O\text{-}n\text{-}Bu)$ (*n*-Bu = butyl ligand) (**3**) were synthesized by reaction of $(\equiv SiO)_3Zr{-}H$ with, respectively, acetylacetone and *n*-butanol at room temperature. Polyoligosilsesquioxane analogues for each of the supported species have also been prepared from the trisilanol, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, to produce tripodal molecular models and from its derivative blocked on two silanol groups, $(c\text{-}C_5H_9)_7Si_8O_{11}(CH_3)_2(OH)$, to provide monopodal models.[13]

Catalytic Tests

Protocol: The liquid phase transesterification of ethyl acrylate by *n*-butanol was chosen as a model reaction to evaluate the performance of the solid catalysts as well as that of their molecular analogues. The reaction was followed to equilibrium at a temperature of around 70 °C with an equimolar amount of ethyl acrylate and *n*-butanol. The catalytic reaction was carried out under argon in the absence of solvent, in a two-necked flask equipped with a condenser. The reaction mixture was composed of ethyl acrylate (4 g, 0.04 mol), *n*-butanol (3 g, 0.04 mol), hydroquinone methyl ether (EMHQ) stabilizer (200 ppm) and the reaction scale was fixed at 8 mL. The amount of catalyst was adjusted to give 4 10^{-5} mol based on zirconium with a BuOH/Zr molar ratio of 1000. In the case of the silica blank, 500 mg of silica previously dehydroxylated at 500 °C were used.

Analysis: The reaction was monitored by taking aliquots (0.1 g) periodically, which were analyzed on a DELSI DI 200 gas chromatograph equipped with a flame ionization detector and a column packed with Chromosorb 101 (1.50 m, 60–80 mesh). Nitrogen was used as gas carrier. Conversion and yield were determined by GC based on relative area of the GC signals referred to an internal standard (octane) calibrated to the corresponding pure compounds ($\Delta_{rel} = \pm 5\%$). GC rate program: 2 min at 100 °C, heating 8 degrees· min^{-1} up to 250 °C, 2 min at 250 °C.

Recycling Procedure

In the recycling studies, fresh catalyst was used as for a standard catalytic run and allowed to react for 6 h. Stirring and heating were removed and the reactor was let stand overnight. The limpid and colourless supernatant was then carefully withdrawn with a syringe and the damp catalyst reused.

Ligands Exchange in Homogeneous Catalysis

Ethyl acrylate (50 g, 0.5 mol), *n*-butanol (37 g, 0.5 mol) and 200 ppm of EMHQ stabilizer were introduced in a Schlenk flask (250 mL) under argon topped with a condenser. The solution was then warmed up at 70 °C before the introduction of $Zr(O\text{-}n\text{-}Bu)_4$ ($5\ 10^{-4}$ mol). After 3 h of reaction a known quantity of ligand was added. The reaction was then followed for another 4 h 30.

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[15] Many variations on protocol and analysis were explored in the pre-study. Final choices were based on a minimal condition of demonstrated reproducibility (less than 2% variance in yield at any point over three independent runs) with the objective of minimizing catalyst use and apparatus complexity. Among the factors studied were 1) comparison of batch results to protocols involving the continuous removal of the ethyl acrylate/ethanol azeotrope; 2) scale of the reaction between 8 mL and 100 mL scale; 3) the effect of the addition of molecular sieves (no effect); 4) the effect of added solvent (dodecane, no significant advantage); and 5) substrate to catalyst ratio (between 100 and 1000).

[16] Neither polymerization nor Michael addition products were observed, perhaps due to the low temperature and the presence of a radical trap (hydroquinone stabilizer).

[17] For simplicity, the relatively inactive $Zr(O\text{-}n\text{-}Bu)_4$ is not represented in Figure 3 and Figure 4. The activity is nearly equivalent to that of the heterogeneous catalysts

3 and **3′**. The allure of the activity of Zr(O-*n*-Bu)$_4$ is represented together with a discussion of its significance in the catalyst regeneration section (see Figure 7 and Figure 8).

[18] Several different exploratory studies of lixivation were performed. These incomplete studies were all equivalent with the hypothesis that some lixivation was present during catalysis with the monopodal catalyst **1** but very little lixivation was observable for **2** and **3**. For example, catalysts **1** and **2** (powders) were tested in the presence of silica beads. Zirconium microanalysis of the beads after reaction showed a similar degree of transfer of zirconium in the case of **1** (~20% transfer), but very little in the case of **2**. In another study, catalyst **1** was continuously extracted (Soxhlet) with butanol for three days (the extraction bed temperature was not measured but was clearly superior to the 70 °C catalytic test temperature): zirconium microanalysis of the solid showed loss of 28% of the initial zirconium.

[19] Accurate quantification of the acetylacetonate would have required very careful study, given the relatively low concentration in the solution coupled with the obvious possibility of chemisorption and physisorption on the silica surface (which itself is undergoing modification during the reaction). The added value of this quantification was not deemed sufficient for the effort required.

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