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Catalytic Properties of Supported Titanates in Transesterification

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Titanates fixed on silica have been employed as catalysts for transesterification of 1-dodecanol with ethyl propionate. Kinetic studies show that the reaction is first order in alcohol by using a semicontinuous reactor and first order in ester by using a batch reactor. Initial rate studies in a batch reactor, where exchange reactions with alcohol and ester are very slow, indicate the influence of the titanium environment on the catalytic activity. The heterogenization of the process shows the importance of hydrolysis, and especially its reversibility, since the catalyst can be regenerated; it also provides a better understanding of the homogeneous experimental conditions because there is no association phenomenon at the surface of the solid.

INTRODUCTION

Titanates have been extensively employed as homogeneous catalysts in esterification and transesterification because they favour high selectivities (1), but they need to be eliminated by hydrolysis and filtration at the end of the reaction. Moreover, their mode of action is practically unknown and kinetic studies have remained relatively unexplored (2).

In the homogeneous system, the activity of the catalyst depends on two factors: these are the titanium environment and the concentration ratios in the equilibrium between a monomeric and a dimeric titanium compound, the monomer form being active and the dimeric one being prevailing and inactive (3).

In a previous work, we investigated the fixation of titanates on alumina or silica supports and their use for the esterification of stearic acid leading to a greater efficiency compared with the homogeneous system (4). The catalyst could be recovered and recycled, and kinetic measurements showed the stability of the titanate–support link (5).

The object of the present work was to use the supported titanates in transesterification. Transesterification was chosen in order to facilitate the kinetic measurements for several reasons: (i) contrary to the esterification reaction, this transesterification is impossible below 120°C without a catalyst, (ii) there is no catalytic effect due to the silica support, and (iii) the absence of H_2O would increase the lifetime of the catalyst.

We studied the reaction of 1-dodecanol with ethyl propionate by following the formation of 1-dodecyl propionate by GC, using two different reactors:

$$C_2H_5COOC_2H_5 + CH_3(CH_2)_{11}OH \rightarrow C_2H_5COO(CH_2)_{11}CH_3 + C_2H_5OH.$$

We also intended to show the influence of the titanium environment on the catalytic activity by using exchange reactions with some alcohols and an acid.

EXPERIMENTAL

All reagents were distilled under argon and dried on a 4-Å molecular sieve before use. The same molecular sieve was used in the reactors; it was previously activated at 200°C under 10^{-4} Torr for 12 h. The silica support (Rhone Poulenc SPH 540; BET specific surface area 277 $m^2\ g^{-1}$; pore volume 0.56 $cm^3\ g^{-1}$; particle size 4–7 mm) was previously dried at 160°C under 10^{-4} Torr for 24 h. The acid strength of the support was estimated by Hammett acidity measurements ($3.3 < H_0 < 4.8$) using basic indicators (6). Gas chromatographic analyses were carried out on an Intersmat IGC 121 instrument equipped with a flame ionization detector using a 25-m Megabor column on BP 624 phase. Titanium titration on the support was determined spectrophotometrically at 410 nm for a complex in H_2O_2 obtained after 12 h reflux in sulfuric acid (7).

Supported catalyst synthesis. Supported catalyst was obtained with a similar procedure as described for esterification reactions (5) by using the reaction of $CH_3Ti(OiPr)_3$ with Brønsted acid sites of silica according to the following reaction:

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$$CH_3Ti(OiPr)_3 + HO\text{-}[Si] \rightarrow CH_4 + [Si]\text{-}O\text{-}Ti(OiPr)_3$$

The reaction was followed by measuring volumetrically the methane production (0.9 CH_4/Ti), and also by the titanium titration on the solid. The supported catalyst denoted as [Si]–Ti–$(OiPr)_3$ in this paper, contained 9 mgTi/g.

Transesterification in a semicontinuous reactor. Dodecanol (164 g; 3 mol L^{-1}) was heated at 120°C in the reactor with the catalyst (16 to 70 g L^{-1}). A semicontinuous reactor was used, as previously described (4), with continuous feed of ester (100 ml h^{-1} flow) at constant temperature (120°C) and under atmospheric pressure leading to a nearly constant concentration of ester (2.6 mol L^{-1}). Continuous distillation of the ethanol formed led to a complete reaction.

Transesterification in a batch reactor. All manipulations were carried out using a high vacuum line and Schlenk technique under argon. The reactor (100 ml) was equipped with a magnetic stirrer and thermostatted at 80°C. In a typical run, stoichiometric amounts (0.1 mol) of ethyl propionate and 1-dodecanol were introduced into the reactor on the 4-Å molecular sieve (2 g). When thermal equilibrium was obtained, the heterogeneous catalyst was introduced (2 g). The reaction mixture was periodically analyzed by GC.

Processing of the catalyst by exchange reactions. [Si]–O–Ti$(OiPr)_3$ catalyst (2 g). The reaction mixture was periodically analyzed by GC.

Processing of the catalyst by exchange reactions. The [Si]–O–Ti$(OiPr)_3$ catalyst (2 g) and 4-Å molecular sieve (2 g) were introduced into a batch reactor. A large excess (20 ml) of reagent (alcohol, acid) was added and the mixture was refluxed under an argon atmosphere for 110 h (20 ml toluene was added as a solvent in the case of exchange with dodecanol). After decantation of the remaining solution, the solid was exhaustively washed with toluene, dried *in vacuo* at 120°C for 16 h, and used for the transesterification test as described above.

RESULTS AND DISCUSSION

Kinetic Studies in the Semi-continuous Reactor

The same reactor was used as described for the esterification of stearic acid by isopropanol, at 120°C instead of 180°C (5). The concentration of the most volatile reagent (viz. ester) used in large excess can be considered as constant (its solubility in the reaction mixture is unchanged during the reaction) and the reaction is driven to completion.

Order with respect to alcohol. The reaction rate law can be written as: $r = k[\text{alcohol}]^{\alpha}[\text{ester}]^{\beta}\,[\text{catal}]^{\gamma}$. On the basis of an order with respect to the heterogeneous catalyst $\gamma = 1$ and keeping the ester concentration constant, we can write

$$r = k'[\text{alcohol}]^{\alpha} \text{ with } k' = k[\text{ester}]^{\beta}[\text{catal}].$$

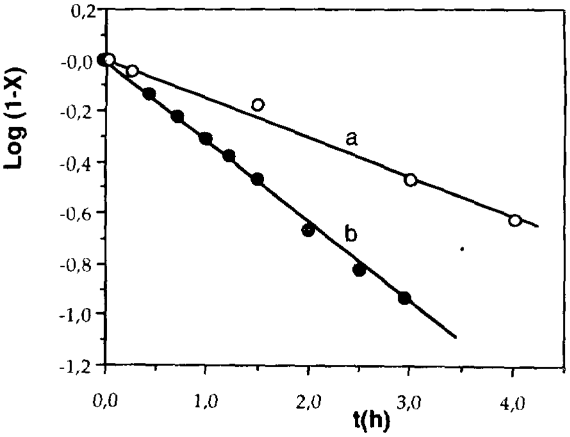

FIG. 1. Diffusion limitations: plot of log (1 − X) versus time (h) in a semicontinuous reactor at 120°C with 5.6 g L^{-1} catalyst amount. (a) Balls; (b) powder from crushed balls.

By using two different amounts of catalyst, we obtained linear plots of log(1 − X) versus time, where X is the conversion and the apparent experimental rate constants were $k' = 3.8$ and $7.2 \times 10^{-3}\ s^{-1}$ for an amount of catalyst of 36 and 71 g L^{-1}, respectively. It is clear that the reaction is first order with respect to alcohol.

The possibility to establish a law indicates that, at low temperature, the catalyst does not undergo any modification by exchange reactions.

Intraparticle and interparticle diffusion limitations. The catalytic activity of the same amount of supported catalyst in the form of silica balls and in the form of powder, obtained from crushed balls, was compared (Fig. 1). An increase was observed in the activity when the size of particles decreased, due to the reduction of intraparticle diffusion limitations.

Interparticle diffusion effects were not present because similar results were obtained by using two different stirring rates.

Effectiveness factors were not calculated because the fixation of the catalyst on the support leads to a lower concentration of titanium inside the pores than on the surface.

Kinetic Studies in the Batch Reactor

Low temperature (80°C) was chosen for work in the batch reactor, in order to render negligible the exchange reactions of the catalyst with alcohol and ester. The con-

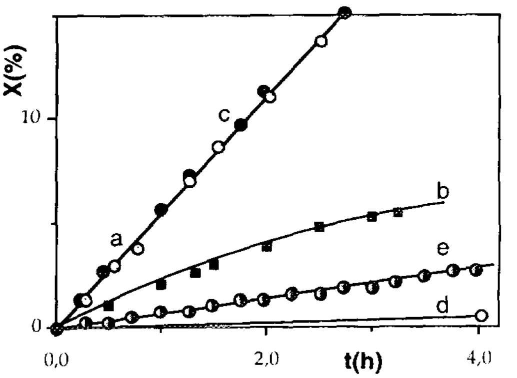

FIG. 2. Conversion versus time (h) in a batch reactor at 80°C with $[Si]\text{–}O\text{–}Ti(OiPr)_3$ catalyst and with [alcohol] = [ester] = 2.9 mol L^{-1}. (a) [cat.] = 50.8 g L^{-1} + sieve (50 g L^{-1}); (b) [cat.] = 53.8 g L^{-1} without sieve; (c) regeneration of (b) by reflux in *i*PrOH + sieve (50 g L^{-1}); (d) sieve alone (140 g L^{-1}); (e) $[Si]\text{–}O\text{–}Ti(OC_{12}H_{25})_3$ catalyst obtained from (a) after 110 h reflux in 1-dodecanol.

version X is a linear function of time as far as $X < 12\%$ (during the first 4 h reaction time).

A molecular sieve was added as recommended by Woodard *et al.* (8) in asymmetric epoxidations catalyzed by titanium tartrates. Indeed, when we first tested the recycling of the catalyst, we observed a 25% loss of activity (whereas titanium titration remained constant) which was due to a partial hydrolysis of the catalyst.

Role of hydrolysis. From transesterification reactions obtained in a batch reactor, it is important to note the different behaviour of heterogeneous and homogeneous catalysts towards hydrolysis. The reaction reported in Fig. 2 confirms that the catalytic activity is inhibited in the absence of a molecular sieve (curve b) and the curved variation obtained implies a modification of the catalyst during the reaction; this fall of activity is connected with a slow hydrolysis of the catalyst, conforming to the reaction

$$[Si]\text{–}O\text{–}Ti(OR)_3 + xH_2O \rightarrow [Si]\text{–}O\text{–}Ti(OR)_{3-x}(OH)_x + xROH. \quad [1]$$

This partial hydrolysis shows the difficulty of drying the reagents in spite of all the precautions we took. When the same amount of the same catalyst is used with molecular sieve, we obtain a linear behaviour (curve a). The molecular sieve alone has no catalytic effect (curve d) and its only function is to remove traces of moisture (9). After recovery, the catalyst used in test (b) was allowed to be refluxed with isopropanol in excess and recycled, after drying, using the same conditions as in test (a). The linear course of the curve (c), fully comparable with curve (a), shows that the partial hydrolysis (Eq. [1]) is reversible and the catalyst is regenerated by reacting with anhydrous alcohol in excess according to the reaction

$$[Si]\text{–}O\text{–}Ti(OR)_{3-x}(OH)_x + xROH \rightarrow [Si]\text{–}O\text{–}Ti(OR)_3 + xH_2O. \quad [2]$$

It is important to note that, although supported titanates are extremely sensitive to hydrolysis like their homogeneous analogues, the process is irreversible with homogeneous systems because of the existence, after the initial hydrolysis, of two bimolecular reactions leading to inactive oxide (10).

$$Ti(OR)_4 + H_2O \leftrightharpoons Ti(OR)_3(OH) + ROH$$

$$Ti(OR)_3(OH) + Ti(OR)_4 \xrightarrow{-ROH} (RO)_3\,Ti\text{–}O\text{–}Ti(OR)_3 \rightarrow TiO_2, xH_2O$$

or

$$2Ti(OR)_3(OH) \xrightarrow{-H_2O} (RO)_3\,Ti\text{–}O\text{–}Ti(OR)_3 \rightarrow TiO_2, xH_2O$$

With supported titanates, only the reversible first step exists, since intermolecular interactions on the surface are unlikely. These results confirm also that the first step of hydrolysis for the homogeneous system really is an equilibrium. Moreover, one can see that the exchange between alkoxy and hydroxy groups has a deactivating effect on the catalytic activity, indicating the importance of the influence of the titanium environment on the activity.

Order with respect to ester. By using the batch reactor at 80°C with a molecular sieve (50 g L^{-1}) and keeping constant the catalyst concentration (50 g L^{-1}), we followed the initial reaction at three different alcohol/ester ratios (0.67, 1, and 1.44). The rate law may be written as

$$r_0 = k'[\text{alcohol}]_0^{\alpha}[\text{ester}]_0^{\beta} \text{ with } \alpha = 1,$$

as explained earlier.

$$r_0 = [\text{alcohol}]_0\, dX/dt,$$

if X is the conversion.

hence $\log(dX/dt) = \beta \log[\text{ester}]_0 + c$, where c is a constant.

The obtaining of linear plots of $\log(dX/dt)$ versus $\log[\text{ester}]_0$ demonstrated that $\beta = 1$. The rate law of transesterification may thus be written as

$$r_0 = k'[\text{alcohol}]_0[\text{ester}]_0 \; [1].$$

Influence of the Titanium Environment on the Catalytic Activity

Kinetic studies of the initial reaction were performed in the batch reactor at low temperature (80°C). The rate law[1] with [alcohol] = [ester] = a_0 is

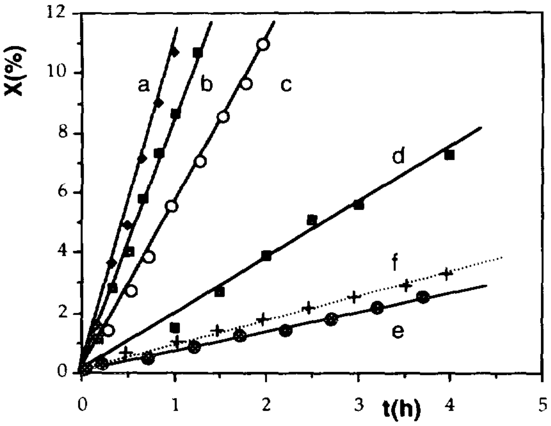

FIG. 3. Conversion versus time (h) in a batch reactor at 80°C with [alcohol] = [ester] = 2.9 mol L^{-1}, [cat.] = 50 g L^{-1} and sieve (50 g L^{-1}) for catalysts obtained after exchange reactions of initial catalyst (c) with (a) CH_3OH, (b) C_2H_5OH, (d) $t\text{-}C_4H_9OH$, (e) $C_{12}H_{25}OH$, and (f) $CH_3CHBrCOOH$.

$$r = k[\text{cat}][a_0]^2 = a_0\, dX/dt, \text{ hence } dX/dt = k[\text{catal}][a_0].$$

The linear variation of the conversion with time indicates that, in these conditions, the environment of titanium is not modified (Fig. 2, curve a); there are no exchange reactions with the reagents (alcohol, ester).

On the other hand, it is possible to modify the environment of titanium by classic exchange reactions at high temperature, over a long period (11). For example, when the initial catalyst [Si]–O–Ti(OiPr)$_3$ (Fig. 2, curve a) is allowed to react with 1-dodecanol at 265°C for 110 h and is used after drying for the esterification test, a linear variation is obtained (Fig. 2, curve e). This exchange reaction with 1-dodecanol was already used to confirm the formula of the catalyst and led to the liberation of 3 mol isopropyl alcohol (5). From the linear behaviour shown in Fig. 2, curve e, it is clear that the new catalyst, corresponding to a dodecyl environment of titanium, presents also a constant reactivity that corresponds to the absence of any modification around titanium during the transesterification.

Thus, kinetic studies of the initial reaction facilitate the study of the catalytic activity of various supported titanates because they are monomers on the surface of the solid.

Figure 3 shows the activity of different catalysts obtained after exchange reactions of the initial catalyst (corresponding to isopropoxy environment around titanium) with some alcohols and an acid.

From the curves of Fig. 3, one can obtain experimental rate constants corresponding to different environments of titanium (see Table 1). These values show clearly the influence of the titanium environment on the catalytic activity which can be due to: (i) an increasing inductive effect which reduces the electrophilic character of the metal or (ii) an increasing steric effect which diminishes the accessibility of the vacant site on titanium.

It can also be noted that a methoxy environment corresponds to the highest activity, whereas Ti(OMe)$_4$, strongly associated, is very difficult to use in the homogeneous system owing to its low solubility (12).

The exchange with 2-bromopropionic acid was chosen to estimate by bromine titration the amount of carboxylate on the surface of the solid after the exchange reaction. This reaction leads to a catalyst formulated as [Si]–O–Ti (OiPr)$_{3-x}$(OCOBrCHCH$_3$)$_x$ with $x = 2.8$ (see Table 1), which is much less reactive (Fig. 3, curve f).

This behaviour explains the practical differences between esterification and transesterification due in fact to a difference of catalyst. These differences are (i) the temperature scale and (ii) the influence of water.

(i) In esterification, the obtaining of carboxylate environment, which decreases the catalytic activity of titanium, necessitates high temperature, in contrast to the alkoxy environment obtained in transesterification. It seems that these differences of activity can be linked to the more or less associated nature of titanates.

Hence, in esterification for homogeneous systems, we always found ½ order with respect to the catalyst, whereas in transesterification one may find first order for low concentration of catalyst (3). This indicates the importance of association in the case of carboxylate environment. In heterogeneous systems, the problem of association does not occur. On the other hand, it is difficult to have all the titanium sites active on a porous support.

(ii) Although H$_2$O is a product of the esterification, the catalyst remains stable during the reaction (providing that water is eliminated by using a semicontinuous reactor); this is due to the slow rate of the hydrolysis of the carboxylate environment (12). On the other hand, in transesterification, the alkoxy environment of titanium, correspond-

TABLE 1

Influence of Titanium Environment on Catalytic Activity of [Si]–O–Ti(OiPr)$_{3-x}$(OR)$_x$ Catalysts

R	*x*	$10^8\,k$ (L mol^{-1} g^{-1} s^{-1})
CH_3	[a]	20.7
C_2H_5	[a]	16.8
$i\text{-}C_3H_7$	3	10.8
$t\text{-}C_4H_9$	[a]	3.7
C_3H_4BrO	2.8	1.5
$C_{12}H_{25}$	3	1.3

[a] Undetermined.

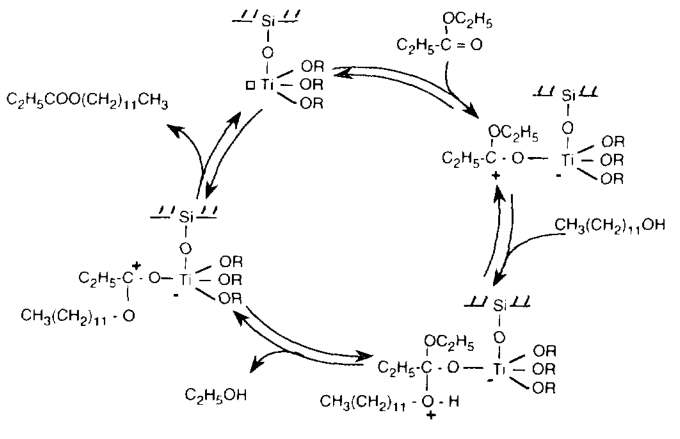

FIG. 4. Suggested catalytic cycle for supported titanate-catalyzed transesterification.

ing to a better Lewis acidity, is more sensitive to hydrolysis.

From the kinetic equation obtained, $r = k$[alcohol][ester][cat.], with first orders with respect to ester and alcohol, we can propose a typically Lewis acid mechanism (13) with successive additions of ester and alcohol (Fig. 4). Nevertheless, the steps and the consequences of this cycle remain to be confirmed.

In conclusion, from a practical point of view, the recycling of the supported catalyst avoids the elimination of the titanate by hydrolysis and filtration at the end of the reaction. In the absence of interparticle diffusion limitations, the order 1 with respect to the catalyst, whatever the concentration used, is more favourable.

From a theoretical point of view, the existence of a monomer titanate on the surface of the support facilitates the study of the influence of the titanium environment on the reactivity of the catalyst. These measurements are impossible with homogeneous systems.

This is well illustrated by the great reactivity of Ti $(OMe)_4$, a catalyst normally unusable in the homogeneous system because of its high degree of association.

It is certain that the nature of the support must also have an influence on the catalytic activity; it would therefore be interesting to use a nonporous support.

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