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Esterification in a structured catalytic reactor with counter-current water removal

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Abstract

In this research the liquid phase esterification of hexanoic acid and 1-octanol was studied. Very high activities were obtained for zeolite BEA and Nafion/silica composite with 13% of Nafion. The advantage of water removal in this system was demonstrated. In a closed system an equilibrium conversion of 35% was reached, while in a system with water removal all the reactants were converted in a shorter period. The initial reaction rate decreases when increasing the initial water concentration, following a Langmuir–Hinshelwood type of rate expression. An active zeolite coated structured monolithic reactor configuration was prepared. Enhancement by the counter-current water stripping of the performance of the structured catalysts was demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Esterification; Kinetics; Structured catalyst; Monolith; Reactive stripping

1. Introduction

The esterification of a carboxylic acid and an alcohol is an example of a solid acid catalysed reaction in which water is formed as a by-product (Fig. 1). The presence of the produced water has two negative effects on the reaction rate: it has an inhibiting effect on the activity of the acidic catalyst and it will limit the maximum obtainable conversion, since the esterification reaction is a reversible, equilibrium limited reaction. Therefore, in situ removal of this produced water will result in a more efficient reactor operation.

The objectives of this study is to demonstrate the benefit of removing the water produced during the reaction and the applicability of a structured catalyst configuration. The liquid phase reaction is carried out over a specifically shaped monolith coated with a solid acid catalyst, and the water is removed by a counter-current stripping operation using a gas flow through the reactor.

Esterifications are industrially relevant reactions. Especially methyl acetate, ethyl acetate and butyl acetate are produced on a large scale [1]. Catalysing the reaction with a solid acid instead of the conventional ones (like mineral acids), has the advantages that the solid acids can be recovered and reused after regeneration, and no corrosive waste streams are produced [2].

Examples of these solid acids are zeolites and ion-exchange resins. Nafion is an ion-exchange resin, which is widely used in water-separation membranes. In its acidic form Nafion can be used as a highly active catalyst for the esterification reaction [3–5]. Zeolites are also active catalysts in acid catalysed reactions, like esterifications [6,7].

In this study a monolith is used as the structured catalyst support. A monolith consists of a macroporous, often cordierite, material that is structured in straight parallel channels. The catalyst is present as a thin layer on the channel walls. Advantages of such a system are

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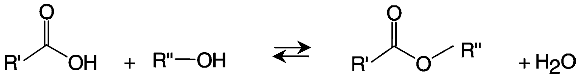

Fig. 1. The esterification of a carboxylic acid with an alcohol.

that no filtering of catalyst is necessary, no attrition of catalyst occurs and the reactor has a low pressure drop. In the case of diffusion limitations, the catalyst is used more efficiently due to the thin catalytic layer present on the cordierite support. A disadvantage is that there is still little practical experience in liquid phase applications. Currently, the most well known application of the monolith is in the automotive industry as an exhaust gas converter. Possible new applications are multi-phase reactions like the solid acid catalysed (two-phase) liquid phase reactions and (three-phase) hydrogenation and oxidation reactions [8]. An example of a study for efficient counter-current removal of a compound in internally finned monoliths (Fig. 2), is the removal of inhibiting H_2S in the hydrodesulfurization of gasoil [9]. In this study internally finned monoliths are being used as a catalyst support for the solid acid catalysed esterification with the counter-current removal of water.

In the finned monolith the liquid is flowing downwards as a thin film along the channel walls, with the gas flowing upwards in the centre (Fig. 3). This is a stripping type of operation because the liquid is not actually boiling and there is no applied temperature gradient over the reactor. In the finned monolith the liquid phase is the reactive part and the gas phase the stripping part. The fins are necessary to stabilise the countercurrent flow, to provide additional surface area for the deposition of the catalyst, and to avoid flooding. Flooding is the phenomenon that the gas velocity is too high compared to the liquid phase velocity resulting in liquid slugs moving upwards in the monolith [10].

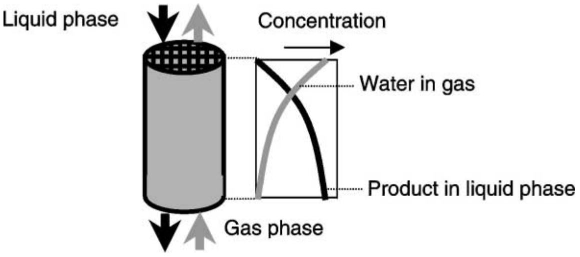

Fig. 3. The counter-current stripping configuration, including the concentration profiles.

2. Experimental

The model test reaction under investigation is the esterification of hexanoic acid with 1-octanol (Fig. 4). For this reaction the activity of various catalysts has been studied. The FAU zeolites with a Si/Al ratio of 5 and 80 were kindly provided by Zeolyst. The BEA zeolite with a Si/Al ratio of 37.5 was purchased from Zeolyst and the BEA zeolites with a Si/Al ratio of 12.5, 25 and 50 were synthesised by Südchemie AG. The Nafion/silica composite with 13% of Nafion was kindly provided by DuPont. All catalysts studied were in the H-form. The activity of the catalysts was studied batchwise in a reflux slurry configuration with the removal of water. The molar ratio in which the hexanoic acid (Merck) and 1-octanol (Baker) were applied was 1:1 and the concentration was $500\,\mathrm{mol\,m^{-3}}$ (7 wt.% of octanol) in cumene. The amount of catalyst used was 0.3 g and the total reaction volume 50 ml. The reaction temperature was 433 K, the pressure was atmospheric and the stirring speed was 500 rpm. For the analysis of the samples, GC–MS was employed with *n*-hexadecane as internal standard.

The effect of water on the reaction system was studied batchwise, using a Nafion/silica composite (13% Nafion) as a catalyst. The slurry-phase reaction is

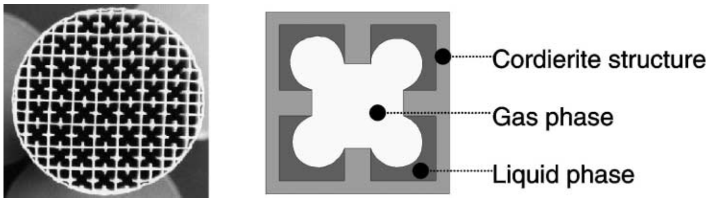

Fig. 2. An internally finned monolith; photographic and a schematic view of a cross-section.

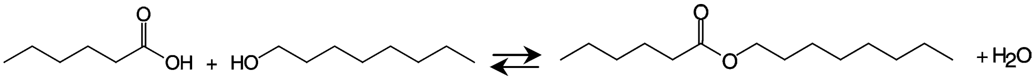

Fig. 4. The esterification of hexanoic acid and 1-octanol.

performed in two reactor configurations. One reactor set-up was the open (reflux) system in which the reaction was performed under removal of water as described above for the catalyst activity measurements. The other reactor set-up was a (micro) autoclave in which the reactions were carried out in a closed system. The volume of the reactor was 10 ml, the reaction temperature 428 K, and the pressure 10 bar nitrogen for sampling. Stirring was accomplished by means of a swinging capillary [11] with a stirring speed of 1000 rpm. In this closed reactor configuration the effect of water was measured by initially adding water to the esterification reaction.

For the application of monolithic structures in the esterification reaction the cordierite monoliths were coated with zeolite BEA. The cordierite structures were kindly provided by Corning. For the coating procedure the cordierite monolithic structures were dipped into a mixture of 2:l water containing 20 wt.% BEA zeolite crystals, 1 wt.% of colloidal silica (Ludox AS40, Aldrich) as a binder and 1 wt.% of Teepol as a surfactant (to stabilise the suspension). The BEA zeolite used for this coating procedure had a Si/Al ratio of 37.5. After dip-coating the structures, a calcination step was executed at 723 K for 4 h. After calcination the structures were ion-exchanged with a 1 M ammonium nitrate solution at 323 K and calcined for a second time at 723 K for 4 h. A 15 wt.% loading of BEA was obtained. The specific activity of this BEA coated monolith was tested on a lab-scale (monolith dimensions: diameter 43 mm, length 50 mm) in a reflux reactor with internal recirculation at atmospheric pressure, see Fig. 5. The reaction conditions (temperature, concentrations) were the same as for the above-mentioned slurry experiments, the only difference being the reactor volume (125 ml).

In all cases the activity was defined as the apparent first-order rate constant k in hexanoic acid normalised for the liquid volume and the amount of catalyst ($\mathrm{m_{liq}^3\ min^{-1}\ g_{cat}^{-1}}$). For the coated monoliths $\mathrm{g_{cat}}$ denotes the amount of catalyst coating in the monolithic support. The real kinetics of this esterification reaction is more complex and will be discussed elsewhere. For the activity of the catalysts the logarithmic plot of the first-order relation ($-\ln(C/C_0)$ vs. time) gives a straight line and works well to compare the performance of the different catalysts.

The activity of the BEA coated internally finned monolith with a length of 2 m and a diameter of 4.3 cm was tested on a pilot scale with recirculation. In this set-up also counter-current water stripping was performed (Fig. 6).

The activity of the coated monoliths was tested in the above-mentioned esterification reaction of hexanoic acid and 1-octanol. The reaction temperature was the same as in the slurry experiments, 433 K. This was achieved by controlling the entire set-up at this temperature, including the vessels and the tubings. Total pressure in the system was 10 bar and total liquid volume was 0.01 $\mathrm{m^3}$. The molar ratio in which the reactants were applied was 1:1 and the concentration

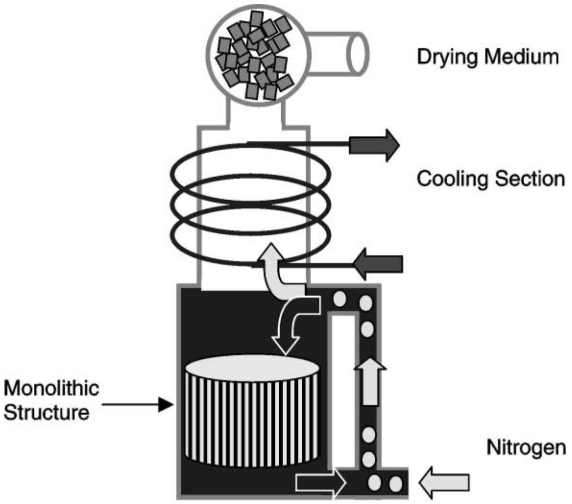

Fig. 5. A schematic picture of the set-up in which the activity of the monoliths are measured.

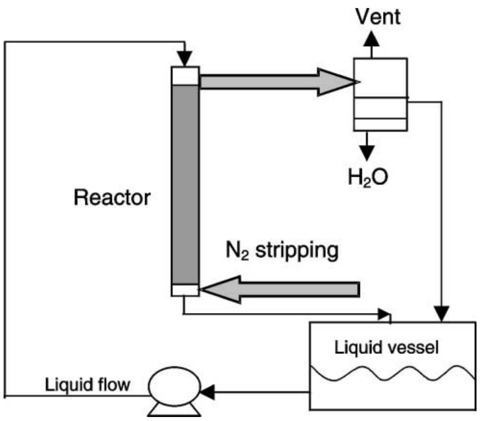

Fig. 6. A schematic view of the pilot reactor set-up.

was 500 mol m^{-3} in toluene. The feed rate of the liquid was 25 kg/h and of the gas 500 Nl/h. With these conditions a hold-up of ∼1.62% in the reactor (the part of the total volume in the monolith) was calculated with the correlations given by Lebens [12].

For the counter-current water stripping application the water produced can be removed very conveniently because water has the lowest boiling point and the highest vapour pressure. The water stripping is achieved in the gas phase by an inert gas (nitrogen) which acts as the stripping agent. After reaction, evaporated product, reactants and solvent can be easily separated from the water, since after condensation (288 K) a phase separation will occur.

3. Results and discussion

The activities of the various catalysts in the esterification of hexanoic acid and 1-octanol are defined as the first-order rate constant in hexanoic acid, and presented in Table 1. Since this refers to an open system where the water is removed by refluxing, the rate constant is indicated by k_0. As the reaction also proceeds without adding a catalyst, the first-order rate constant of this reaction is given, too. To give an indication of the achieved conversion after a certain time the conversion of the acid is given. The selectivity given is the selectivity towards the formed ester. The other main product formed is an ether as a result of an etherification reaction between two alcohol molecules.

The BEA zeolites and the Nafion/silica composite with 13 wt.% of Nafion give similar activities. Compared to the esterification reaction without a catalyst the reaction rate is increased by a factor of 15–20. The activities of the faujasites are very low. Apparently these catalysts are not active enough for catalysing this esterification reaction. Since the particle sizes of the faujasites are smaller (approximately 3.5 μm) than the particle sizes of the BEA zeolites (approximately 7 μm), this difference cannot be due to external transport limitations. Internal transport limitations can also be excluded, because the channel sizes are similar (7.4 Å for FAU and 5.5 Å × 5.5 Å and 7.6 Å × 6.4 Å for BEA). Therefore, this difference between the two types of zeolites must be the result of differences in

Table 1
The activities and selectivities of various solid acid catalysts in the esterification of hexanoic acid with 1-octanol as measured in a slurry reactor[a]

Catalyst	k_0 (10^{-6} m^3 min^{-1} g$_{\mathrm{cat}}^{-1}$)	Conversion of hexanoic acid (%)	Selectivity (%)
No catalyst added	0.2[b]	25% after 300 min	99[c]
BEA (Si/Al = 12.5)	3.6	100% after 150 min	92
BEA (Si/Al = 25)	4.5	100% after 150 min	94
BEA (Si/Al = 37.5)	3.7	100% after 150 min	94
BEA (Si/Al = 50)	3.5	100% after 150 min	93
FAU (Si/Al = 2.5)	0.7	60% after 300 min	88[c]
FAU (Si/Al = 40)	0.5	60% after 300 min	94[c]
SAC13	3.5	100% after 90 min	97

[a] Activity (10^{-6} m^3 min^{-1} g$_{\mathrm{cat}}^{-1}$) is defined as the apparent first-order reaction coefficient (min^{-1}) normalised for the catalyst concentration (total liquid volume divided by the total amount of catalyst; m^3 g$_{\mathrm{cat}}^{-1}$). Selectivity (%) is defined towards the formed ester at 100% conversion of the acid.

[b] Activity of the esterification without any additional solid catalyst is defined as the apparent first-order reaction coefficient (min^{-1}).

[c] Selectivity (%) after 300 min.

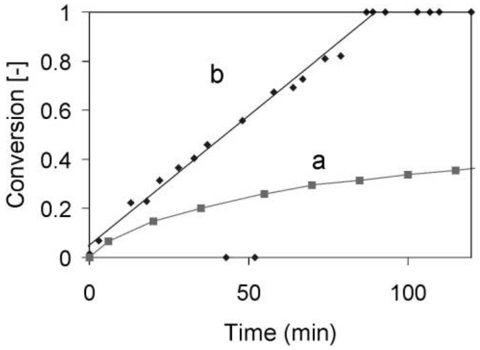

Fig. 7. The conversion of hexanoic acid in the Nafion/silica composite catalysed esterification of hexanoic acid with 1-octanol: (a) in a closed system (autoclave); (b) under removal of water.

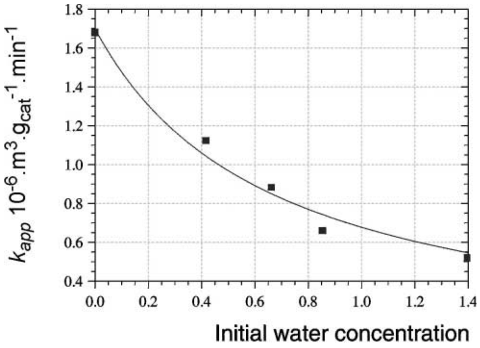

Fig. 8. The effect of initially added water on the apparent initial first-order rate constant k_{app}. Markers: experimental results, line: Langmuir–Hinshelwood relation (Eq. (1)).

activity of the catalytic sites. Finally, it must be noted that hardly any effect of the Si/Al ratio on the activity was observed. Since the Si/Al ratio has an effect on the amount of acid sites and the acid strength [13], a more detailed study of the acidity of the zeolites is required to investigate this aspect.

The selectivity of the catalysts towards the formed ester is in all cases very high. As a result of adding a catalyst the selectivity decreases from 99% to approximately 90%, probably due to the formation of ethers over the strongly acidic catalytic sites. The highest selectivity is obtained by the Nafion/silica composite with 13 wt.% of Nafion.

The conversion of the acid is given in Fig. 7. The slurry-phase reaction is performed in a closed system and under removal of water. It can be seen that with water removal the conversion of the acid reached 100% just after 90 min, whereas the closed system did not even attain equilibrium after 120 min. Therefore, the advantage of the removal of the water is clearly demonstrated.

In the closed system, also some experiments were performed with water addition. The effect of this water on the apparent first-order reaction rate constant is given in Fig. 8. The apparent initial rate constant evidently decreases with increasing initial water concentration. If a Langmuir–Hinshelwood type of expression is considered the following equation (see Eq. (1)) can be applied and subsequently a value for the adsorption term of water can be fitted.

$$k_{\mathrm{app}} = k_0 \frac{1}{1 + K_{\mathrm{W}} c_{\mathrm{W}_0}} \qquad (1)$$

with k_{app} ($\mathrm{m^3\,g_{cat}^{-1}\,min^{-1}}$) for the initial reaction rate constant, k_0 ($\mathrm{mol\,m^3\,g_{cat}^{-1}\,min^{-1}}$) for the initial reaction rate constant in the absence of water, K_{W} ($\mathrm{m^3\,mol^{-1}}$) for the adsorption constant of water, and ($\mathrm{m^3\,mol^{-1}}$) for the initial concentration of water.

This fitted reaction rate dependency on the adsorption of water is depicted in Fig. 8, evidencing the rate inhibition by competitive water adsorption.

The activity of this BEA-coated monolith was tested in the above-mentioned esterification reaction in the labscale reflux reactor. The activity achieved was $2.4 \times 10^{-3}\,\mathrm{m^3\,min^{-1}\,g_{cat}^{-1}}$, which is slightly lower than the k obtained in the slurry phase for the same catalyst ($3.1 \times 10^{-3}\,\mathrm{m^3\,min^{-1}\,g_{cat}^{-1}}$). The results of the esterification experiments in the BEA-coated monolithic pilot scale reactor of 2 m length and 4.3 cm diameter are given in Fig. 9. Again the reaction without any catalyst was measured as well as the reaction in the presence of a bare cordierite monolith.

A very active zeolite coated monolith has been prepared, because the zeolite coated structures exhibit a much higher activities than the esterification reaction without or with a bare cordierite monolith. The latter two experiments exhibited similar activities as the slurry experiments in which no catalyst was added. With catalyst, the conversion per one pass of the liquid flow was 26–30%.

For comparison between stripping and no-stripping the conversion at (for example) 130 min is considered. At this point the conversion is about 0.87 in the stripping configuration compared to 0.75 in the no-stripping configuration, clearly demonstrating the

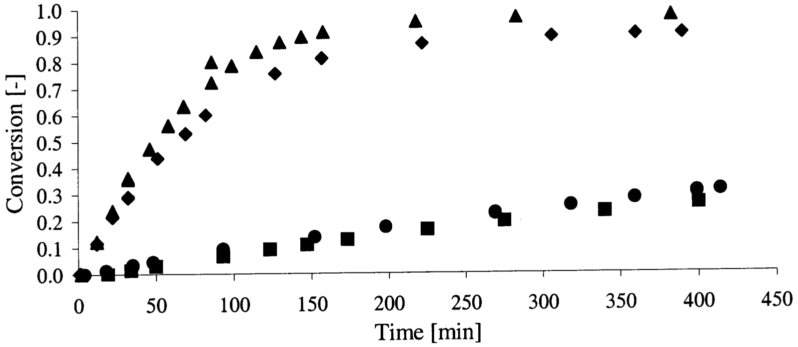

Fig. 9. The effect of counter-current stripping on the conversion of hexanoic acid in the esterification reaction performed on a BEA coated monolith. (■) Reaction, without any catalyst added, with stripping. (●) Reaction, in the presence of an uncoated monolith, with stripping. (◆) Reaction catalysed by a BEA coated internally finned monolith. (▲) Reaction catalysed by a BEA coated internally finned monolith, with counter-current water stripping.

enhancement of the counter-current water stripping on the performance of the structured catalysts.

The high conversion levels reached even without stripping in the pilot scale reactor compared to the slurry experiments in a closed reactor can be easily explained. In the slurry experiments the gas phase volume was about 20% of the total reactor volume while in the case of the pilot scale reactor this was about 90%. Since the amount of water in the liquid phase is proportional to the vapour pressure of water (being 6.2 bar at the temperature of 433 K), it can be calculated that nearly all the water formed in the case of the closed reactor experiments listed in Fig. 7, is present in the liquid phase, whereas most of the produced water in the pilot scale experiments is present in the gas phase, pushing the reversible reaction towards the right.

In these pilot scale experiments, selectivities of 85 and 87% were obtained at 100% of conversion for the stripping and the no-stripping configuration, respectively. The reference experiments (no catalyst, with and without bare cordierite monolith) gave 100% of selectivity, analogous to the slurry experiments.

4. Conclusions

In the reaction of hexanoic acid and 1-octanol over solid acid catalysts, zeolite BEA and Nafion/silica composite with 13% of Nafion gave the highest activity (with an activity expressed as the apparent first-order reaction coefficient of $k = 17\text{–}20 \times 10^{-6}\,\mathrm{m^3\,min^{-1}\,g_{cat}^{-1}}$), being much higher than for the reaction rate without a catalyst. The selectivity towards the formed ester is in all cases >90%, the main side reaction being the etherification of the alcohol. The advantage of water removal is clearly demonstrated, in a closed system an equilibrium is not even reached after 400 min, whereas in a system with water removal all the reactants were converted just after 120 min. The initial reaction rate decreases when increasing the initial water concentration, following a Langmuir–Hinshelwood type of expression.

The activity of BEA coated monolithic structures was slightly lower ($2.4 \times 10^{-6}\,\mathrm{m^3\,min^{-1}\,g_{cat}^{-1}}$) than the k obtained in the slurry reactor ($3.1 \times 10^{-6}\,\mathrm{m^3\,min^{-1}\,g_{cat}^{-1}}$). The activity of these BEA coated structures gave also high conversions on a pilot scale. On this latter scale the enhancement was shown of the counter-current water stripping on the performance of the structured catalysts.

Acknowledgements

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