

# Kinetics of solid acid catalysed etherification of symmetrical primary alcohols: zeolite BEA catalysed etherification of 1-octanol

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## Abstract

The etherification of 1-octanol catalysed by zeolite BEA was investigated. The kinetics were determined in an open system with almost no water present. The influence of the catalyst particle size, catalyst concentration, temperature, and alcohol concentration was investigated. The apparent activation energy measured for the etherification was 149.8 kJ/mol. The 1-octanol showed an inhibiting effect on the reaction rate, i.e. when the concentration of 1-octanol increased the initial reaction rate decreased. This effect can be explained by a Langmuir–Hinshelwood like mechanism in which an adsorbed alcohol needs an empty neighbouring site to form an active intermediate and split of water. The influence of water on the kinetics was investigated using a closed autoclave set-up. Water showed a strong inhibiting effect on the initial reaction rate of the etherification of 1-octanol.

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## 1. Introduction

The etherification of symmetrical primary alcohols is an acid catalysed reaction used in the fine chemical industry. The produced ethers are stable and can easily dissolve organic substances. Therefore, they can for example be used as emulsifier in cosmetic products [1]. Another, bulk chemical, application of symmetrical long chain ethers is as an additive for diesel fuels. Adding about 0.5–5.0% (w/w) of ether can enhance the cetane number of diesel up to 15%, consequently resulting in cleaner burning of the diesel [2,3].

The most common method to produce ethers is the Williamson syntheses. This involves the reaction of an alkyl halide and a basic alkoxide in which a stoichiometric amount of waste salts is produced. These form the major drawback of the Williamson synthesis [4]. In the specific case of symmetrical ethers the alcohols can be dehydrated with strong acid catalysts, for example sulphuric acid, at elevated temperatures [2,5,6]. A disadvantage of this homogeneous

method is the separation of the catalyst and product after reaction, which leads to large corrosive waste streams. A more attractive method for the preparation of ethers is the use of solid acid catalysts, like inorganic acids, clays, ion-exchange resins, and zeolites. Inorganic solid acids like aluminas [7–12], silica–aluminas [8], and aluminium phosphates [13] have been applied in the dehydration of 1-butanol. Another inorganic solid acid frequently encountered in literature is ion-exchanged montmorillonite [6,14,15]. Ion-exchange resin catalysts, especially Nafion-H and Amberlyst-15, are used in industrial ether synthesis [2,5,16]. The disadvantage of the use of ion-exchange catalysts is the thermal instability, causing corrosion problems. Zeolites, like zeolite Y, X, BEA and ZSM-5, offer an interesting alternative [16–19]. The Brønsted acidity of the zeolites is subscribed to the protons adsorbed on the bridging oxygen atoms of the  $\equiv\text{Al}-\text{O}^- - \text{Si}\equiv$  group. The Al atoms are the source of the Brønsted acidity. Changing the  $\text{Si}_2\text{O}:\text{Al}_2\text{O}_3$  ratio thus varies the amount of acid sites. However, it must be noted that the strength of the acid sites decreases with an increase in Al atoms.

Brown [20] applied zeolite BEA in the etherification of symmetrical secondary alcohols. In the synthesis

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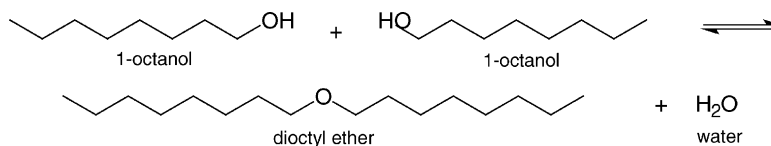


Fig. 1. The etherification of 1-octanol to di-octylether.

of methyl-*tert* butyl ether (MTBE) from methanol and iso-butene zeolite BEA showed a comparable activity to the current commercial ion-exchange resin Amberlyst-15 [21–23]. Other zeolite catalysts (i.e. zeolite Y and ZSM-5) showed substantially lower activity. The good performance of zeolite BEA was subscribed to the high external surface area, whereas Hunger and Horvath [24] explained it to be a result of the adsorption of methanol on the silanol groups of the zeolite BEA. This is in contrast to zeolite Y and ZSM-5 in which the methanol is mainly adsorbed on the bridging OH groups.

The use of zeolite BEA as a catalyst in the etherification of symmetrical primary alcohols has not been discussed in literature. In this research we studied the zeolite BEA catalysed etherification of 1-octanol, Fig. 1. The reaction kinetics were investigated using an open system from which almost all water was removed. Furthermore, the influence of water on the reaction kinetics was investigated in a closed system in which water remained present.

## 2. Experimental

### 2.1. Catalysts

The kinetics were determined using a commercial zeolite BEA (CP811E-75) with a SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of 75:1 from Zeolyst International. Ground extrudates of the same zeolite BEA were used for the examination of the effect of the particle size. These extrudates were also provided by Zeolyst International. Before each test the amount of catalyst necessary was calcined at 823 K for 4 h and kept dry at 393 K until use. In Table 1, the properties of the zeolite BEA catalysts are listed.

### 2.2. Chemicals and apparatus

The reactant 1-octanol (99.5%, Fluka) and the solvent cumene (99%, Acros Chemicals) were used as received. A

Table 1  
Properties of the zeolite BEA catalysts

	Particle size $d_p$ (m)	Surface area $S_{BET}$ (m <sup>2</sup> /g)	Pore volume $V_{pore}$ (ml/g)
BEA extrudates	$3 \times 10^{-3a}$	580	0.9
BEA powder	$8 \times 10^{-6b}$	640	1.1

<sup>a</sup> Diameter of the extrudates.

<sup>b</sup> Size of the crystal clusters.

small amount of tetradecane (99%, Acros Chemicals) was added as an internal standard for gas chromatographic analysis of the samples taken during the experiments. The GC analysis were done with a Varian CP3380 gas chromatograph equipped with a 1177 FID detector, Varian CP8400 auto sampler, and a CP-SIL-8 column (length 60 m, internal diameter 0.25 mm, and film thickness 0.25 μm). The temperature program of the gas chromatograph starts at 323 K followed by heating with 10 K/min until 523 K. This end temperature was maintained for 10 min.

### 2.3. Experimental set-up open system

The open reflux set-up consists of six glass slurry reactors with a volume of 100 ml. The reactors, schematically shown in Fig. 2, were equipped with a glass stirrer and a reflux cooler including a drying tube on top containing silica gel to maximize the removal of water [25]. The experiments in the glass reactors were performed batch wise at reflux conditions (430 K) and atmospheric pressure. Experiments with different stirrer speeds were done to verify if external mass transfer limitation occurs.

In the glass reactors about 75 ml of cumene was used. The concentration of 1-octanol in this system was varied between 100 and 1500 mol/m<sup>3</sup>, and the catalyst concentration between 0 and 9 kg/m<sup>3</sup>. The standard concentrations used are 300 mol/m<sup>3</sup> of 1-octanol and 4 kg/m<sup>3</sup> of zeolite BEA. The sieve fractions of zeolite BEA particles used are <63 μm, 63–125 μm, 125–212 μm, 212–355 μm, and 355–500 μm.

### 2.4. Experimental set-up closed system

The closed set-up was a 500 ml titanium autoclave, schematically shown in Fig. 3, from Premex Reactor

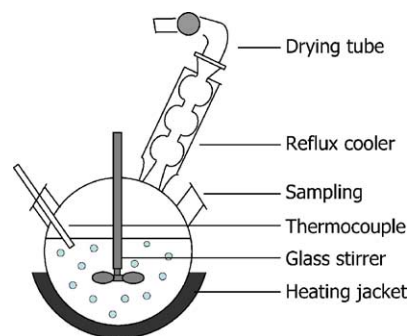


Fig. 2. Schematic representation of one of the glass reactors in which the kinetic parameters in an open system were measured.

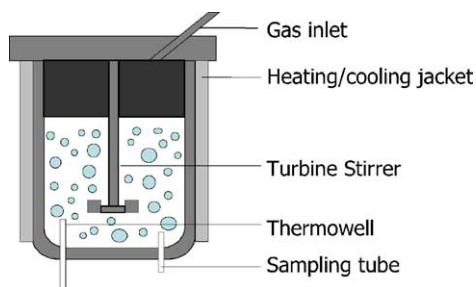


Fig. 3. Schematic representation of the autoclave set-up in which the kinetic parameters in a closed system were measured.

AG Switzerland. The autoclave was equipped with a magnedrive, a titanium Rushton turbine stirrer, a thermowell, and a heating and cooling jacket located in the reactor wall. The experiments in this autoclave were performed batch wise at 423 K and  $9 \times 10^5$  Pa nitrogen. The nitrogen pressure is needed for sampling. The stirrer speed was set at 1000 rpm.

In the autoclave about 270 ml of cumene was used. The concentration of water in this system was varied between 0 and  $300 \text{ mol/m}^3$ . The standard concentrations used are  $300 \text{ mol/m}^3$  of 1-octanol and  $4 \text{ kg/m}^3$  of zeolite BEA.

### 2.5. Kinetic measurements

In a plot of the concentration of 1-octanol versus time, the initial slope of the 1-octanol concentration represents the initial reaction rate. To take into account the experimental error in the weighing of the catalyst the initial reaction rate is normalised for the amount of catalyst.

## 3. Results and discussion

### 3.1. Influence of the stirrer speed

In Fig. 4, the influence of the stirrer speed on the activity is shown. From the figure, it can be seen that there is already

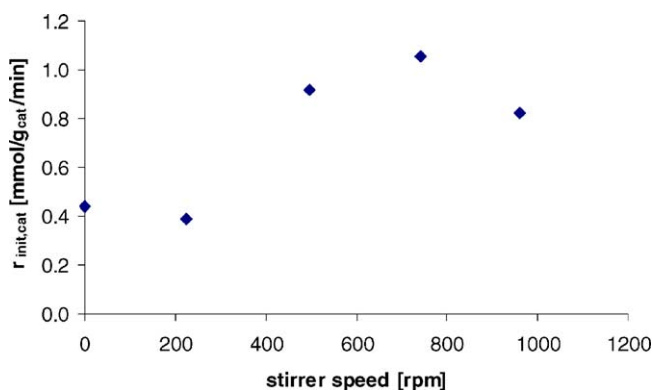


Fig. 4. The effect of the stirrer speed on the initial reaction rate. Tests performed in the glass reactors at  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA, 430 K, and atmospheric pressure.

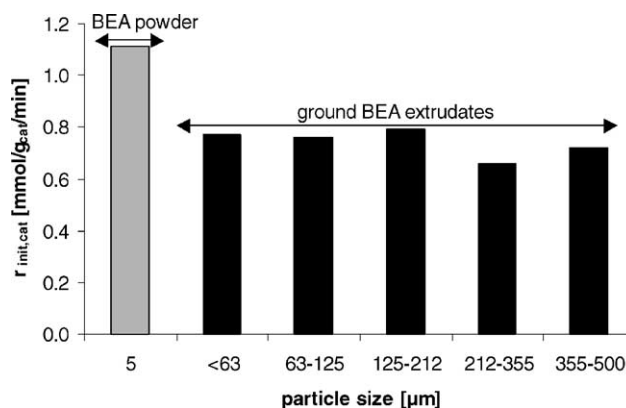


Fig. 5. The effect of the particle size of the zeolite BEA on the initial reaction rate. Tests performed in the glass reactors at  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA, 430 K, and atmospheric pressure. The gray bar shows the activity of the zeolite BEA powder, while the black bars show the activities of the ground extrudates of zeolite BEA.

substantial activity when no stirring is applied. This is due to the reflux conditions used, that is the boiling of liquids causes enough movement to mix the zeolite BEA particles and the liquid in such a way that reaction can occur. The activity is not longer masked by external mass transfer limitations at a stirrer speed of 500 rpm or higher. For the kinetic measurements, a stirrer speed of 500 rpm was used in all the experiments.

### 3.2. Influence of the zeolite BEA particle size

In Fig. 5, the effect of the particle size on the activity is shown. The powder of the zeolite as used in the kinetic measurements is shown in grey, while the different particle sizes of the ground extrudates are shown in black. As can be seen from the figure the activity of the powder is higher than for the ground extrudates. This is due to the binder that is added in order to make the extrudates out of the zeolite BEA powder. From Table 1, it is clear that this binder causes a decrease in the surface area. This results in a lower accessibility of the acid sites of the zeolite BEA particles. If we compare the activities for the sieve fractions, i.e. different particle sizes of the ground extrudates it is clear that there is no significant change in the activity with the different particle sizes. From this, it can be concluded that there are no internal mass transfer limitations.

### 3.3. Effect of the temperature

The etherification reaction was also performed at different temperatures, namely 390, 400, 420, and 430 K. The results are depicted in an Arrhenius plot, Fig. 6, to calculate the apparent activation energy. From the slope of the plot ( $= -E_a/R$ ) follows that the apparent activation energy equals  $149.8 \text{ kJ/mol}$ . This value supports the conclusion that there are no internal and external mass transfer limitations.

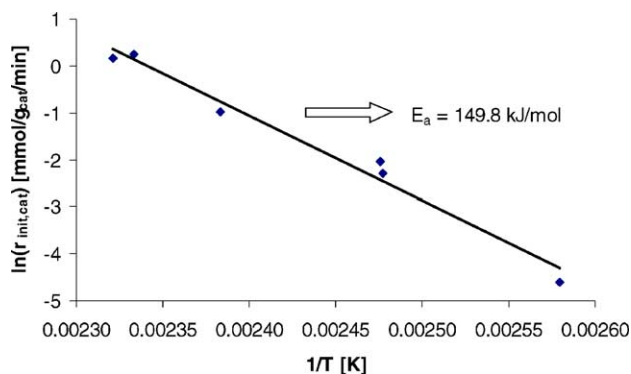


Fig. 6. Arrhenius plot of the etherification of 1-octanol catalysed by zeolite BEA. Tests performed in the glass reactors at 300 mol/m<sup>3</sup> octanol, 4 kg/m<sup>3</sup> BEA, and atmospheric pressure.

This makes it possible to measure the intrinsic reaction kinetics of the etherification. The apparent activation energy measured is in accordance with the results found by Collignon et al. [23] in the etherification of methanol and iso-butene over zeolite BEA. They measured apparent activation energies between 94 and 158 kJ/mol, depending on the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite BEA used. The high value of the apparent activation energy means that there is a high dependence of the reaction rate on the temperature. Therefore, the results for the experiments are all normalised, using this activation energy, for the temperature differences that occur.

### 3.4. Kinetics with water removal

#### 3.4.1. Influence of the catalyst concentration

Fig. 7 shows the influence of the zeolite BEA concentration on the initial reaction rate of the etherification of 1-octanol. These raw data were not normalised to the amount of catalyst present. From the figure, it can be seen that no reaction takes place when there is no catalyst present. Fur-

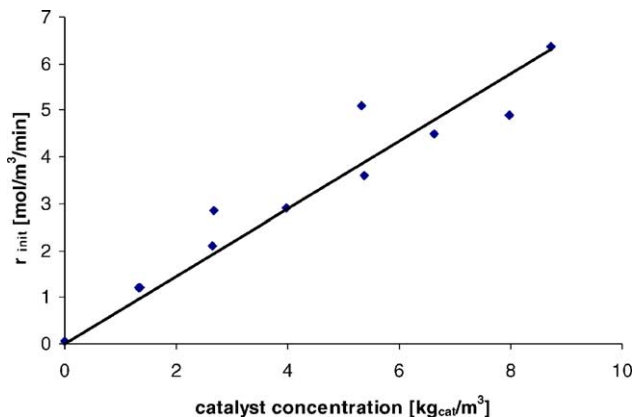


Fig. 7. The effect of the zeolite BEA concentration on the initial reaction rate of the etherification of 1-octanol. Tests performed in the glass reactors at 300 mol/m<sup>3</sup> octanol, 430 K, and atmospheric pressure.

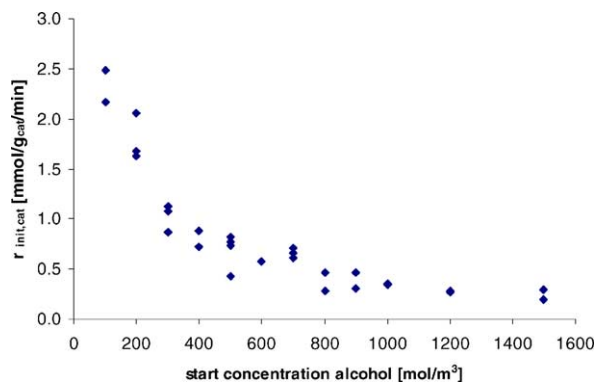


Fig. 8. The effect of the start concentration of octanol on the initial reaction rate in the etherification reaction catalysed by zeolite BEA. Tests performed in the glass reactors at 4 kg/m<sup>3</sup> BEA, 430 K, and atmospheric pressure.

thermore, it can be seen that the etherification is first order in the zeolite BEA concentration. A first order in the catalyst concentration is expected in heterogeneous catalysis when substances in the feed do not poison the active sites.

#### 3.4.2. Influence of the 1-octanol concentration

Fig. 8 shows the change in the initial reaction rate as a function of the initial alcohol concentration at standard conditions. As can be seen from the figure, with an increasing initial alcohol concentration the activity decreases. For example, when the initial 1-octanol concentration is five times higher (500 instead of 100 mol/m<sup>3</sup>) the activity of the etherification is approximately three times lower (0.8 instead of 2.4 mmol/(g<sub>cat</sub> min)). So when the catalyst surface is fully covered with alcohol the reaction rate is lower than in the case of a partially covered catalyst surface. This indicates some kind of inhibiting effect of the reactant itself, i.e. the alcohol 1-octanol. A similar behaviour was observed by Françoise and Thyron [26] for the ethanol reactant in the synthesis of ethyl *tert*-butyl ether catalysed by Amberlyst-15. They subscribed this to the occurrence of two different mechanisms depending on the concentration of ethanol. At a high ethanol concentration the proton site would become solvated, i.e. become a weaker acid site. Nunan et al. [27] found a maximum in the reaction rate with an increasing iso-butanol concentration in the dehydration of iso-butanol towards iso-butene over a Nafion-H catalyst. A dual site mechanism was proposed in which an empty catalytic site was involved. However, the etherification reactions of methanol and iso-butanol did not show this effect.

#### 3.4.3. Proposed kinetic model

The inhibiting effect of the 1-octanol in the etherification can be explained by a mechanism in which empty sites are necessary for the conversion of the alcohol. This empty site is used by a neighbouring adsorbed alcohol to split of water and form a reactive intermediate. When the alcohol concentration increases the number of empty catalytic sites decreases. Consequently, the reaction rate drops with

increasing alcohol concentration. This can be modelled by the reaction scheme as presented in Eqs. (1)–(5). The following elementary steps are considered to take place successively at the surface of the zeolite BEA:



So first 1-octanol is adsorbed on the surface of zeolite BEA, as shown in step one. In the second step it can be seen that an adsorbed molecule of 1-octanol needs a free catalytic site to convert into an intermediate reactant and split of water at the same time. The intermediate, subsequently, reacts with a free 1-octanol molecule to form the octyl ether, step three. The products that are being formed, water and ether, can desorb from the surface, shown in steps four and five.

The intermediate that is being formed in step two immediately reacts with a free alcohol to form the ether and does not desorb from the catalyst surface. In other words, the reactions two and three run in series. To explain the effect of the start concentration of 1-octanol, it is assumed that the surface reaction is the rate-determining step.

Summarising, the assumptions that have been made are: (i) the reaction takes place on identical sites at the surface; (ii) the surface reaction step two is the rate determining step; (iii) the intermediate concentration on the surface is almost zero; (iv) steps two and three run in series; (v) the adsorption of reactants and products is reversible.

The individual elementary steps can be described by the following reaction rate equations:

$$r_1 = k_1 c_a N_t \theta_* - k_{-1} N_t q_a \quad (6)$$

$$r_2 = k_2 S N_t \theta_a q_* \quad (7)$$

$$r_3 = k_3 N_t \theta_m c_a \quad (8)$$

$$r_4 = k_4 c_w N_t q_* - k_{-4} N_t \theta_w \quad (9)$$

$$r_5 = k_5 c_e N_t q_* - k_{-5} N_t \theta_e \quad (10)$$

In which  $k_i$  are the reaction rate constants,  $c_i$  the concentrations,  $\theta_i$  the surface coverage,  $N_t$  the total number of sites, and  $S$  represents the number of neighbouring sites of an active site.

It is assumed that the adsorption of reactants and products is in quasi-equilibrium, steps 6, 9, and 10. In other words, the surface concentrations are directly related to the concentrations in the liquid phase:

$$K_i = \frac{k_i}{k_{-i}} = \frac{\theta_i}{c_i \theta_*} \quad (11)$$

Eq. (7) in combination with the assumptions leads to the following Langmuir–Hinshelwood like rate expression:

$$r = r_2 = \frac{k_2 K_a c_a c_{cat}}{(1 + c_a K_a + c_e K_e + c_w K_w)^2} \quad (12)$$

In which  $K_a$ ,  $K_e$ , and  $K_w$  represent the adsorption constants of respectively the alcohol, ether, and water. The following simplifications are made:  $N_t$  can be described by the concentration of catalyst and  $S$  is taken into account by the reaction rate constant.

#### 3.4.4. Fitting of the model parameters

The use of an elevated temperature and drying tubes ensures the removal of almost all water from the reaction mixture in the open system. In the case of a negligible concentration of water the model of Eq. (12) can be simplified to:

$$r = \frac{k_2 K_a c_a c_{cat}}{(1 + c_a K_a + c_e K_e)^2} \quad (13)$$

If one considers the initial reaction rate, when no ether is formed yet, Eq. (13) reduces to:

$$r_{init} = \frac{k_2 K_a c_a c_{cat}}{(1 + c_a K_a)^2} \quad (14)$$

Eq. (14) can be fitted on the initial reaction rates of the 25 experiments with different starting concentrations of 1-octanol as depicted in Fig. 8. The result for the reaction rate constant is then used in the fitting of the kinetic model of Eq. (13). This model was simultaneously fitted to a collection of 25 experiments, each consisting of 10–15 data points. The experiments used had different starting concentrations of alcohol and were performed in the glass reactor set-up, which is an open system. These two steps were repeated until the values for the kinetic parameters did not change significantly. The model was fitted using a non-linear Bayesian estimation method with a single response, namely the alcohol concentration. The computer program Athena Visual Workbench version 8.2 was used for the fitting of the kinetic model.

The results of the fit for a selection of four different start concentrations, in total nine experiments, are shown in Fig. 9. The experimental data shows a good agreement with the fitted model in all the experiments. The results for the kinetic parameters are given in Table 2 together with their confidence intervals. The values for the adsorption coefficients show that the ether adsorbs approximately two times stronger than the alcohol on the surface of zeolite BEA.

Table 2  
Results of the fit of the kinetic parameters without water present

Parameter	Value	95% confidence interval	Units
$k_2$	0.0102	±0.0007	mol/(g <sub>cat</sub> min)
$K_a$	0.0154	±0.0016	m <sup>3</sup> /mol
$K_e$	0.0264	±0.0019	m <sup>3</sup> /mol



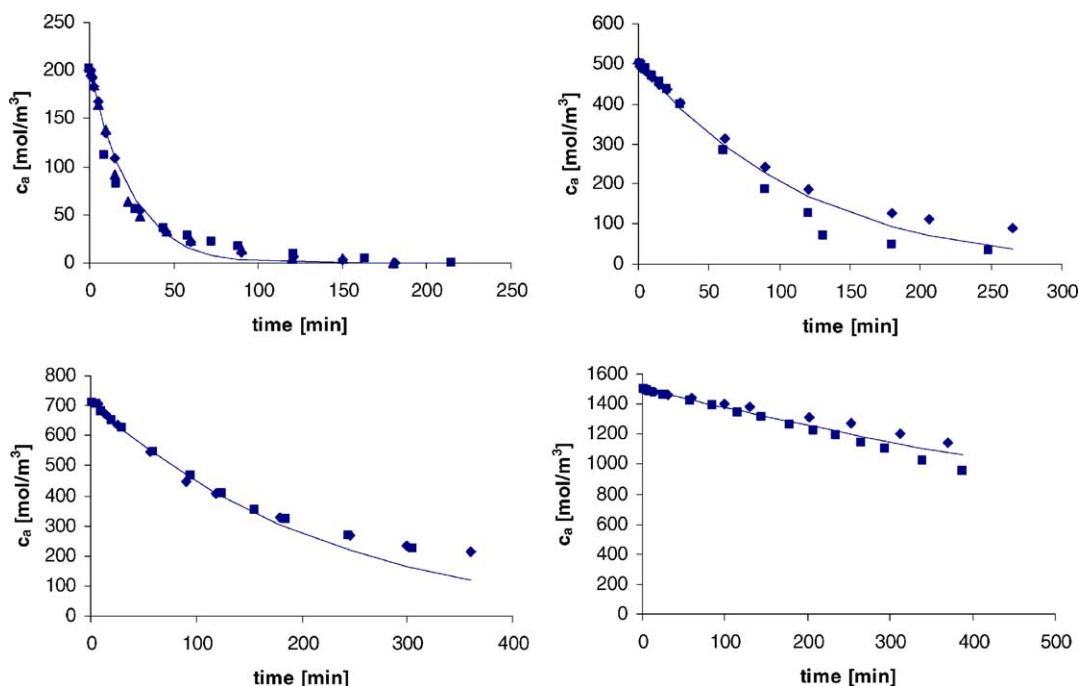


Fig. 9. The results of the fit for experiments with different starting concentrations of alcohol. (■, ◆) Different experimental results; (—) fitted model. Tests performed in the glass reactors at  $4 \text{ kg/m}^3$  BEA, 430 K, and atmospheric pressure.

### 3.5. The effect of water on the reaction kinetics

#### 3.5.1. Influence of initial water concentration

During the etherification water is being formed. This is known to adsorb strongly on the catalytic sites of a solid acid catalyst, like zeolite BEA [28]. Yin et al. [29] found an inhibiting effect of water on the initial reaction rate in the etherification of ethanol and *tert*-butyl alcohol over both a heteropoly acid and Amberlyst-15 as a catalyst. The reaction rate decreased up to 17 times depending on the catalyst and temperature.

In the glass reactors used to determine the kinetics, the water produced is almost completely removed from the solution by the use of an elevated temperature and drying tubes. To study the effect of water experiments were done in an autoclave reactor, Fig. 2, which is a closed system. With Karl Fisher it was measured that there is approximately  $20 \text{ mol/m}^3$  water already present in the reaction mixture of cumene, 1-octanol, and tetradecane before adding any additional water. Furthermore, experiments were performed with an extra of 50, 100, 200, and  $300 \text{ mol/m}^3$  water. The autoclave experiments have been performed at a slightly lower temperature than the glass reactor experiments. In order to be able to compare the different activities the initial reaction rates were normalised with the help of the apparent activation energy.

The results for the autoclave experiments are shown in Fig. 10. It can be seen that the activity in the autoclave without extra water added,  $0.165 \text{ mmol}/(\text{g}_{\text{cat}} \text{ min})$ , is about six times lower than for the experiments in the glass reactor,

$1.024 \text{ mmol}/(\text{g}_{\text{cat}} \text{ min})$ . Additional adding of water further increases the initial reaction rate with a factor of two. Adding more than  $50 \text{ mol/m}^3$  of water initially has no further effect on the initial reaction rate.

#### 3.5.2. Fitting of the kinetic parameters

The initial reaction rate has been used to fit the kinetic model with water present. Due to the water present Eq. (14) cannot be used, but Eq. (13) can be simplified to the following equation:

$$r_{\text{init}} = \frac{k_2 K_a c_a c_{\text{cat}}}{(1 + c_a K_a + c_w K_w)^2} \quad (15)$$

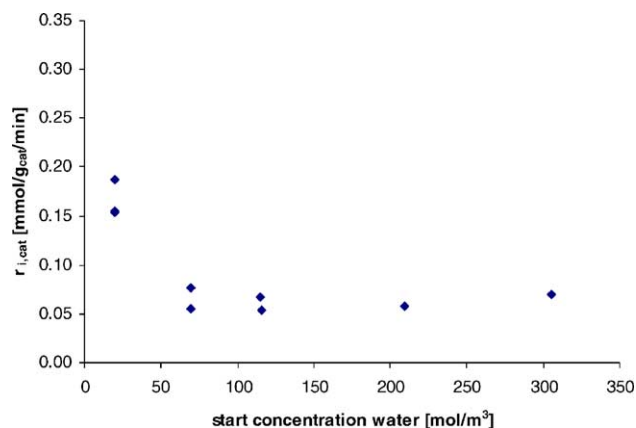


Fig. 10. The effect of the start concentration of water on the initial reaction rate for the etherification of 1-octanol. Tests performed in the autoclave at 423 K,  $9 \times 10^5 \text{ Pa N}_2$ ,  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA.

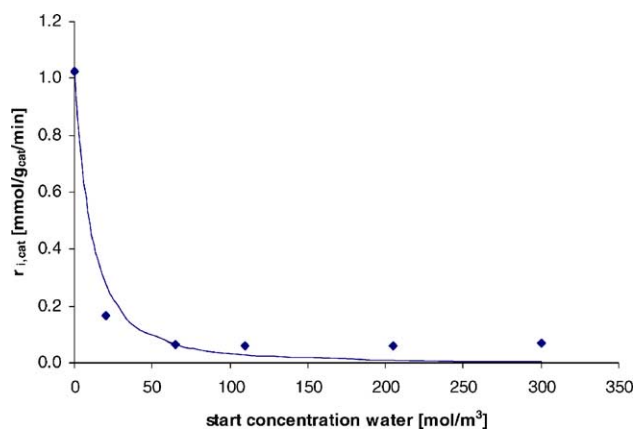


Fig. 11. The results of the fit for the initial reaction rate with different starting concentrations of water. (◆) Experimental results; (—) fitted model. Tests with initial water present are performed in the autoclave at 423 K,  $9 \times 10^5$  Pa  $N_2$ ,  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA. Tests without water present are done in the glass reactors at  $300 \text{ mol/m}^3$ ,  $4 \text{ kg/m}^3$  BEA, 430 K, and atmospheric pressure.

This Eq. (15) was fitted on the eight experiments shown in Fig. 10 together with the three experiments for the glass reactors at a start concentration of  $300 \text{ mol/m}^3$ , which represents the initial reaction rate at a start concentration of water of  $0 \text{ mol/m}^3$ . The values for the adsorption constants for the alcohol and ether were set to the values found for the kinetic model without water, see Table 2. The model was again fitted using a non-linear Bayesian estimation method with a single response, namely the alcohol concentration.

The result for the fit of the kinetic model is shown in Fig. 11. This time the points represent the average of the experiments as shown in Fig. 10 and the point at a zero start concentration of water is also shown. The data corresponding to the lower concentrations of water are well described by the model. The model begins to deviate from the data points above a start concentration of  $50 \text{ mol/m}^3$  water. For the model the initial reaction rate keeps decreasing with increasing start concentration of water, while the experimental values become constant. A possible explanation for this difference between the model and experimental data could be the change in the acidity of the catalytic site due to the adsorption of water. In other words, there could be two different mechanisms playing a role in the etherification with water present. In Fig. 12, these two mechanisms are illustrated. Without water the protons adsorbed on the bridging oxygen atoms are forming the acid site. When water adsorbs on the acid site a  $H_3O^+$  is being formed. This adsorbed water could now function as a new catalytic site, but with a weaker acidity resulting in a lower activity. This activity will become constant when the complete surface of zeolite BEA is saturated with water. For the adsorption of water on the  $H^+$  site the adsorption constant  $K_w$  is approximately  $0.6 \text{ m}^3/\text{mol}$ . That is around 20–40 times higher than for the ether and alcohol, see Table 2. The description of the data with one model combining the two mechanisms requires

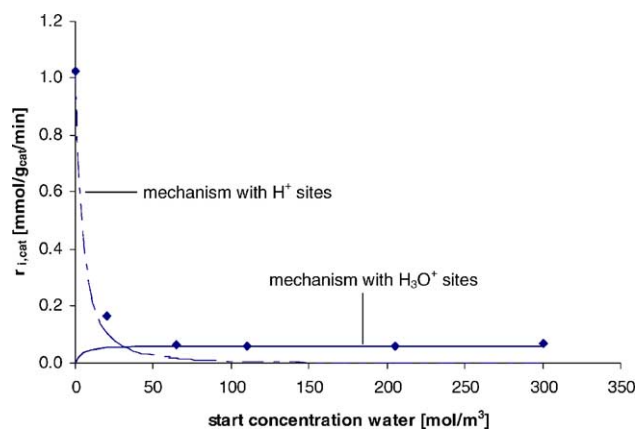


Fig. 12. The two mechanisms for the initial reaction rate with different starting concentrations of water. (◆) Experimental results; (—) mechanism with  $H_3O^+$  sites; (---) mechanism with  $H^+$  sites. Tests with initial water present are performed in the autoclave at 423 K,  $9 \times 10^5$  Pa  $N_2$ ,  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA. Tests without water present are done in the glass reactors at  $300 \text{ mol/m}^3$  octanol,  $4 \text{ kg/m}^3$  BEA, 430 K, and atmospheric pressure.

knowledge about the effect of the alcohol on the kinetics with water present. More measurements would be needed to exactly determine the effect of the water, however these are outside the scope of the current research.

#### 4. Conclusions

The kinetics of the etherification of 1-octanol catalysed by zeolite BEA is measured in an open system, where almost no water is present in the reaction mixture. By changing the reaction temperature, it is found that the apparent activation energy equals  $149.8 \text{ kJ/mol}$ . Furthermore, upon changing the particle size the reaction rate keeps constant. These findings show that under the conditions used the kinetics can be measured without being masked by internal or external mass transfer limitations.

The etherification shows a decrease in initial reaction rate when the initial concentration of 1-octanol was increased. This inhibiting effect is explained by using a mechanism in which an adsorbed alcohol molecule needs an empty neighbouring catalytic site to form a reactive intermediate and split of water. A Langmuir–Hinshelwood like rate expression can then describe the kinetics of the etherification of 1-octanol.

The effect of water on the reaction kinetics is investigated using a closed system. Water shows an inhibiting effect on the reaction rate. The initial reaction rate decreased approximately 10 times when  $50 \text{ mol/m}^3$  water was added to the reaction mixture. Further adding of water had no more influence on the initial reaction rate. This is explained by the possible change in catalytic site due to the adsorption of water. In this case two different mechanisms play a role corresponding to the initial  $H^+$ -sites and the  $H_3O^+$  sites formed after adsorption of water.

### Nomenclature

$c_{\text{cat}}$	concentration of catalyst ( $\text{kg}/\text{m}^3$ )
$c_i$	concentration of component i ( $\text{mol}/\text{m}^3$ )
$E_a$	activation energy ( $\text{kJ}/\text{mol}$ )
$g_{\text{cat}}$	mass of catalyst (g)
$k_i$	reaction rate constant ( $\text{mol}/\text{g}_{\text{cat}} \text{ min}$ )
$K_i$	adsorption constant ( $\text{m}^3/\text{mol}$ )
$N_t$	total number of sites
$p$	pressure (Pa)
$r_i$	reaction rate ( $\text{mol}/\text{m}^3 \text{ min}$ )
$r_{\text{init}}$	initial reaction rate ( $\text{mol}/\text{m}^3 \text{ min}$ )
$r_{\text{init,cat}}$	initial reaction rate normalised with catalyst concentration ( $\text{mmol}/\text{g}_{\text{cat}} \text{ min}$ )
$S$	number of neighbours of an active site
$T$	temperature (K)
$\theta$	catalytic site

### Subscripts

a	alcohol
e	ether
m	reaction intermediate
w	water
*	vacant site

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