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Zeolite BEA catalysed esterification of hexanoic acid with 1-octanol: Kinetics, side reactions and the role of water

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ABSTRACT

In recent years, solid acid catalysts such as zeolite BEA are increasingly applied in esterification and etherification reactions, especially in reactive distillation and reactive stripping. In this study, the kinetics of the zeolite BEA catalysed esterification of 1-octanol with hexanoic acid and its side reaction, the etherification of 1-octanol, has been determined. Both reactions can be described using a Langmuir–Hinshelwood type approach accounting for the reversibility of the esterification reaction, limiting the conversion level. The influence of the water concentration on the esterification kinetics was investigated using a closed reactor system. The adsorption of water is 38 times stronger than that of 1-octanol while the adsorption of hexanoic acid, ester and ether are negligible. The formation of octene is not considered in the kinetic model as it was found that octene is formed by ether splitting when mass transfer limitations play a role. Therefore its formation is negligible in kinetic experiments using a powder catalyst.

The kinetic parameters determined in this study allowed direct prediction of the instantaneous selectivity as a function of the reaction coordinate of the esterification and of the fraction of water removed. These predictions were validated by data from pilot scale reactive stripping experiments.

1. Introduction

In recent years, solid acid catalysts have found increased application in esterification and etherification reactions. Their main advantages in comparison to conventional mineral acids are that they are non-corrosive and easy to separate from the reaction mixture for reuse. If fixed on structured supports, such as Multipak, Katapak-S or film flow monoliths, integration of reaction and separation becomes possible to overcome equilibrium limitations, e.g. in reactive distillation [1,2] or reactive stripping [3–5].

Besides resins (e.g. Amberlyst®) and superacids such as sulphonated zirconia, several zeolites have been investigated in the past. Zeolite BEA (beta, H-BEA) has been used in the esterification of acetic acid with butanol [6,7], in the etherification of glycerol with isobutene [8], and of 2-naphthol with ethanol [9]. Hoek et al. [10] successfully applied zeolite BEA as catalyst for the etherification of 1-octanol. Beers et al. [3] and Nijhuis et al. [11] investigated the use of zeolite BEA in structured reactors for the esterification of hexanoic acid with 1-octanol with water removal.

An accurate kinetic model will enable further insight by modeling/simulation (e.g. the prediction of the selectivity as a function of the alcohol conversion and water removal) in the use of reactive stripping reactors for the esterification of hexanoic acid.

One of the challenges in determining kinetic parameters for the esterification over solid acid catalysts is the proper handling of the water concentration. The water present in the reaction mixture limits the conversion not only due to the thermodynamic equilibrium, but also by strongly adsorbing on the active catalytic sites. It has been shown that water removal can enhance the conversion strongly [11]. Most authors assume a water concentration of zero since they run the reaction in a boiling solvent, at temperatures above the boiling point of water, but with reflux condensation.

The aim of this study is to investigate the role of water and to determine one set of kinetic parameters describing the zeolite BEA catalysed esterification of 1-hexanol and octanol together with the main side reaction, the etherification of 1-octanol (see Fig. 1).

2. Experimental

2.1. Experiments in glass reactors

The water concentrations in experiments similar to those presented in [10,11] have been determined by taking liquid samples at different times and subsequent analysis by Karl–Fischer

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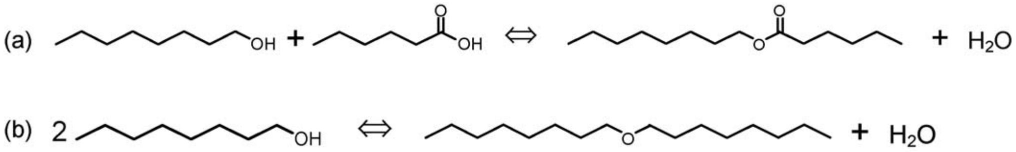

Fig. 1. (a) Reaction scheme esterification of hexanoic acid and octanol-1. (b) Reaction scheme etherification of octanol-1.

Coulometry. For these tests, stirred glass flasks equipped with a reflux cooler were run at atmospheric pressure and reflux conditions (160 °C using 40 ml of cumene as the solvent). The optimal stirrer speed was determined before carrying out the reported experiments by repeating experimental runs with different stirrer speeds. The initial liquid concentrations were varied between 0.1 and 1.2 mol/l for 1-octanol and 0.45–1.35 mol/l for hexanoic acid. The catalyst hold-up was 2.75 g/l of a commercial zeolite BEA (CP811E-75) with a SiO_2:Al_2O_3 ratio of 75:1 (from Zeolyst International).

Besides powder catalyst, complete and powdered extrudates of the same zeolite BEA (also from Zeolyst International) were used to examine the effect of the particle size. Pieces of BEA coating on cordierite monoliths (coating procedure described in [12]) were used for the examination of the effect of the coating procedure on the activity. 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.

The reactants 1-octanol (99.5%, Fluka, density 824 kg/m^3) and hexanoic acid (99%, density 920 kg/m^3) and the solvent cumene (99%, Acros Chemicals, density 862 kg/m^3) were used as received. A 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 analyses 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.

2.2. Experiments in autoclave reactor

For the experiments with suppressed water removal and therefore increased water content, a 5 cm long piece of BEA coated monolith (diameter 43 mm) was mounted in a 500 ml autoclave. The coating procedure has been described elsewhere [12]. The liquid concentrations were 0.91 mol/l of 1-octanol, 0.90 mol/l of hexanoic acid. The catalyst hold-up was 4.85 g/l and the total liquid hold-up was 268 ml. The experiments were performed at a temperature of 160 °C and a pressure of 0.67 MPa. To maintain gradient-less operation, a turbine type stirrer (speed about 1000 rpm which was high enough to ensure mixing) circulated the liquid very fast through the monolith channels. During the experiments, liquid samples were taken from the reactor and analysed by GC and Karl–Fischer Coulometry as described above.

Table 1
Properties of BEA catalysts.

	Particle size (m)	Surface area (m^2/g)	Pore volume (ml/g)
BEA extrudates	1.5×10^{-3}[a]	580	0.9
BEA powder	8×10^{-6}[b]	640	1.1
BEA coating (pieces)	0.5×10^{-3}[c]		

[a] Diameter of extrudates.
[b] Size of crystal cluster.
[c] Thickness of coating.

3. Results and discussion

Fig. 2 shows the initial octanol conversions in glass reactor experiments (160 °C, 0.75 mol/l of hexanoic acid and 0.75 mol/l of 1-octanol, 2.75 g/l of BEA), measured for the original BEA powder, BEA-extrudates (ca. 12 mm long, 1.5 mm diameter), powdered extrudates and samples from BEA coating. It can be observed that the rates do not differ too much (maximum 20% deviation of the slopes). Internal (pore) diffusion limitation and the coating procedure seem to have only a slight negative impact on the activity in the case of monoliths.

For all the glass reactor experiments, similar to those presented in [10,11], water concentrations between 0.003 mol/l and 0.001 mol/l were measured. This indicates that the water cannot be removed completely under the reflux conditions applied. One important reason is that the vapour–liquid-equilibrium constant for water changes significantly when organic compounds containing functional groups like 1-octanol and hexanoic acid are added to the system water–cumene [13]. Therefore, these concentrations were added to the experimental data used for the determination of kinetic parameters.

Fig. 3 shows typical results of an autoclave experiment: the conversion of hexanoic acid, the amount of water expected based on the conversion and the amount of water determined by KF-coulometry. Not all expected water is detected in the liquid. About half of the water is present either in the vapour phase or condensed as droplets at the cool points of the autoclave set-up, e.g. in the tubing leading to pressure indicators, etc. Therefore, it is important to use only measured water concentrations for the determination of kinetic parameters.

Moreover, during the experiment it was observed that liquid samples containing more than 5000 ppm of water show clouding (i.e. signs of formation of a second phase) even if they are hot (>70 °C). When a water phase segregates from the organic phase within the reactor, the interpretation of the water effects becomes

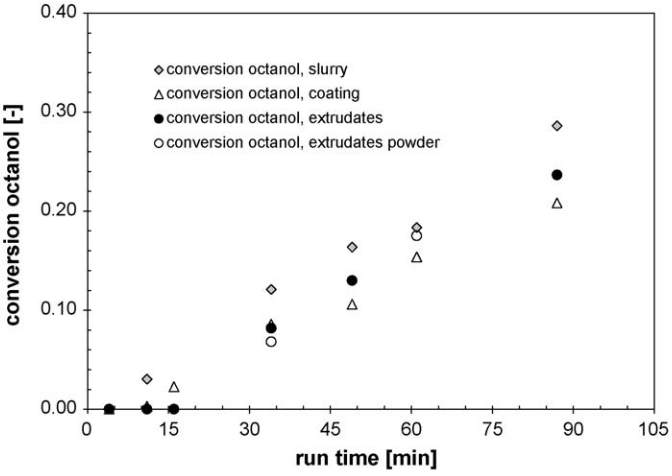

Fig. 2. Initial octanol conversions in glass reactor experiments for different forms of BEA catalyst (160 °C, 0.75 mol/l of hexanoic acid and 0.75 mol/l of 1-octanol, 2.75 g/l of BEA).