Solid acid catalysed conversions of oleochemicals
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SUMMARY

In this thesis two heterogeneously catalysed reactions that are important in the oleochemical industry are treated. In chapter 2 and 3, an investigation into the heterogeneously catalysed dimerisation of unsaturated fatty acids is described. Esterification, a key reaction in oleochemistry, is the subject of chapters 4 to 6.

Chapter 2 is entitled ‘Active sites in the montmorillonite catalysed dimerisation of unsaturated fatty acids’. The superior catalytic activity of montmorillonite clay in the dimerisation of unsaturated fatty acids is not well understood. In this chapter, investigations into the relative importance of the various acid sites as well as structural and textural parameters of montmorillonite for the dimerisation of oleic acid are described. It is shown that reaction in the interlamellar space dominates the oleic acid dimerisation. The active site is the tetrahedral substitution site, and the influence of the type of interlayer cation on the activity of montmorillonite is explained in terms of its effect on the interlayer distance. Model catalysts with mesopores and tetrahedral substitution sites do not show any activity in oleic acid dimerisation. A dual site adsorption of oleic acid, i.e. requiring the presence of both interlayer cations (arising from octahedral substitution) and tetrahedral substitution sites, is proposed as explanation for the superior activity of montmorillonite.

Chapter 3 continues on the investigations into the clay catalysed dimerisation of oleic acid. Montmorillonite clay has a unique activity in the dimerisation of unsaturated fatty acids. In Chapter 2, dual site adsorption was proposed to explain this superior catalytic activity. The carboxylic group is thought to co-ordinate to the interlayer metal cations and the activation of the double bond occurs at the tetrahedral substitution site.

In this chapter, the hypothesis that reaction takes place in the interlayer of the clay catalyst is further validated. To this end, experiments with addition of water and ethylene
glycol are conducted. Further a range of synthetic clays was synthesised in order to vary systematically the extent of tetrahedral substitution, which was proposed previously to generate the active sites for the reaction of the carbon-carbon double bond.

In Chapter 4 the reaction studied is the esterification reaction, focussing on activity and selectivity of silica-alumina catalysts in gas phase esterification of acetic acid and ethanol. Esters form an important product category, for instance for the synthesis of intermediates for fragrances, flavors and detergents. Mostly esterification reactions are carried out in batch processes using homogeneous catalysts. In the search for potentially better solid acid catalysts, the influence of acidic properties of a variety of silica-alumina based solid acid catalysts on the activity and selectivity is studied. To this end the gas phase esterification of ethanol and acetic acid is used as a model system and is investigated by means of a combination of NH$_3$-TPD and kinetic studies. The catalysts studied include microporous zeolite Beta and H-ZSM-5, mesoporous silica-alumina MCM-41, and amorphous silica-alumina catalysts, all with a varying Si/Al ratio. The major side reactions, i.e. ethanol dehydration towards diethyl ether and ethene, are independently studied as well. It is demonstrated that the esterification reaction predominantly proceeds over strongly acidic sites. The selectivity of reaction is found to depend both on the conversion and on the acetic acid to ethanol molar ratio, but not on the acidity of the active sites. Ethanol dehydration is shown to proceed over both weakly and strongly acidic sites and is promoted by a high Al content in silica-aluminas.

In Chapter 5 the mechanism of the gas-phase esterification of acetic acid and ethanol over MCM-41 is investigated in more detail. Whereas the mechanism for the homogeneously catalysed esterification is long known, this does not hold for the esterification over heterogeneous catalysts. Using transient and steady state experiments, temperature programmed desorption (TPD), and using isotopic labelling experiments, the esterification
mechanism over MCM-41 (Si/Al = 16) is studied. Gas phase esterification of acetic acid with ethanol over MCM-41 (Si/Al = 16) is shown to proceed via a Langmuir-Hinshelwood type mechanism, involving a protonated acetic acid intermediate.

In Chapter 6, the impact of catalyst acidity and hydrophobicity on the activity of zeolite Beta in esterification reactions is investigated. A number of zeolitic materials with a varying Si-to-Al ratio were tested in both liquid phase and gas phase esterification reactions. Thereby the impact of the acid site distribution and the hydrophilic nature of these catalysts were systematically assessed. It is shown that in liquid phase esterification both the surface hydrophobicity, the polar nature of the reactants and the acid strength of the solid acids are key factors in esterification. Hydrophilic materials are shown to be inactive in the liquid phase esterification of apolar substrates. This may be ascribed to strong adsorption of water formed during the reaction, leading to inhibition by counteracting the adsorption of reactants onto the active sites. More polar substrates compete more effectively with water for the adsorption sites and thus for these substrates the influence of the hydrophobicity of the catalyst on its activity becomes less pronounced.

In contrast to what is observed in liquid phase esterification, in gas phase esterification the influence of the catalyst hydrophobicity is small or even absent. In these reactions the activity depends largely on the number of acidic sites and acid strength distribution of the catalyst.