SUMMARY

The hydration of lower alkenes to produce the corresponding alkanols is carried out industrially on a large scale. The hydration reaction is acid catalyzed and yields secondary or tertiary alkanols, except, of course, when ethene is used. Both homogeneous and heterogeneous catalysts are used. In the conventional (homogeneously catalyzed) two-step process the alkene is absorbed in concentrated sulfuric acid in the first step, leading to the formation of the alkyl sulfate. In the second step this sulfate is hydrolyzed using an excess of water, yielding the corresponding alkanol and dilute sulfuric acid. The recombination of this acid is an energy consuming and polluting process, proceeding under very corrosive conditions. These factors are serious drawbacks of the two-step, so-called indirect hydration process. An advantage of the indirect hydration process is that feeds of low alkene content can be used.

The direct hydration of alkenes may be performed in a one-step process using a heterogeneous catalyst. Highly active heterogeneous catalysts are strong acid ion exchange resins. The application of these catalysts to the hydration of propene is of considerable industrial importance. However, very few results of fundamental research on the use of ion exchangers as catalysts are available.

The aim of the study described in this thesis is to obtain several basic engineering data on the hydration reactions and the ion exchange catalysts. Little attention is given to the hydration of ethene, as the temperature required for a reasonable rate of hydration is well above the thermal stability limit of commercial ion exchange resins.

In Chapter 2 kinetic experiments on the hydration of propene are described. The results are explained by a reaction model with the isopropyl carbonium ion as intermediate. Reaction rate constants of the formation of this intermediate from propene, 2-propanol and diisopropyl ether (a side-product formed in the hydration reaction) have been determined in a fixed bed plug-flow reactor, packed with ion exchange particles. A water-rich liquid phase is the only fluid phase present in the reactor. Reaction rate constants have been determined in the temperature range 85 - 130°C. The chemical equilibrium constants, expressed in liquid phase concentrations, have been determined in the temperature range 100 to 150°C.

The rate of formation of isopropyl carbonium ions from propene is about one order of magnitude larger than from 2-propanol or diisopropyl ether. In the temperature range investigated the carbonium ions formed are mainly converted
to 2-propanol. The rate of formation of the carbonium ion from the reactants decreases with increasing 2-propanol content of the liquid, which is ascribed to a medium effect.

A typical value of the equilibrium ratio of 2-propanol and propene in the water-rich liquid phase at 130°C is 70. The enthalpy of formation of 2-propanol from propene and water in the water-rich liquid phase is about -55.0 kJ.mol⁻¹. The enthalpy of formation of diisopropyl ether from 2-propanol is -10.8 kJ.mol⁻¹. The fraction of diisopropyl ether present at equilibrium increases rapidly with increasing 2-propanol content of the liquid. At a particle size of 0.8 mm, typical of commercial ion exchangers, intraparticle diffusional limitations have to be taken into account at temperatures over about 130°C.

Chapter 3 describes the corresponding experiments for the butene hydration system. Simultaneously with the formation of 2-butanol isomerization of the butenes (1-butene, cis-2-butene and trans-2-butene) takes place, as expected with a sec-butyl carbonium ion intermediate. Chemical equilibria in the butene hydration system are less favorable for the formation of alkanol than in the propene system. The equilibrium ratios, expressed in liquid phase concentrations, of 2-butanol and the three butenes (in the order mentioned above) at 130°C are: 166, 35.3 and 24.0, respectively. The overall equilibrium constant, defined as the ratio of 2-butanol and the sum of the three butenes, is even lower: 13.2 at 130°C.

Reaction rate constants of the formation of the intermediate carbonium ion from alkenes and alkanols are in the same range in the propene and butene hydration system. Activation energies for these reactions are about 110 and 150 kJ.mol⁻¹, respectively. The enthalpies of formation of 2-butanol from the butenes 1-butene, cis-2-butene and trans-2-butene are -48.5, -38.6 and -36.5 kJ.mol⁻¹, respectively.

In Chapter 4 experimental results on the phase equilibria involved in the propene and butene hydration systems are presented for temperatures in the range 130 to 160°C and pressures in the range 6 - 9 MPa. The solubility of propene in the water-rich phase increases with increasing temperature, pressure and 2-propanol content of the water-rich liquid phase. The distribution coefficient of 2-propanol in the 2-propanol - propene - water system, defined as the ratio of the mole fraction of 2-propanol in the propene- water-rich phase, is in the range of 4 - 7. The corresponding value of 2-butanol in the butene system is in the range of 20 - 30. Increasing temperature and decreasing pressure lead to a reduction in these distribution coefficients. The distribution coefficients of the ethers diisopropyl ether and di-sec-butyl ether are...
very large (> 100) in these systems, especially at low alkanol content of the water-rich liquid phase.

In Chapter 5, 6 and 7 the properties of strong acid ion exchange resins are discussed with respect to their use in a hydration reactor.

Chapter 5 describes the determination of effective diffusion coefficients ($D_e$) and solubilities of lower alkenes in water-swollen resins in the absence of reaction. Experiments have been performed at atmospheric pressure and temperatures in the range 10 - 60°C. The partition coefficient ($\lambda$) of alkenes over ion exchange resins and water, defined as the ratio of the solubility of the alkene in the water-swollen resin and in water, is only slightly temperature dependent. The $\lambda$-values for the lower alkenes are in the range 1 - 3. The effective diffusion coefficients have been determined by measuring the instationary sorption behaviour of lower alkenes in these resins. It appeared that the instationary sorption curve can be described by a single value of $D_e$. A linear relation exists between $\ln D_e$ and 1/T. The apparent energy of activation of diffusion is about 25 kJ.mol$^{-1}$, independent of the alkene used. The value depends on the ionic form of the resin used.

The ratio of the diffusion coefficient of the alkenes used in water ($D$) and the effective diffusion coefficient in a resin ($D_e$) ranges from 6 - 20 at ambient temperature for resins in the H$^+$-form. The lowest values of this ratio are obtained with macroporous resins. The highest values for the larger molecules (butenes) with geltype resins. An equation is presented which seems suitable to correlate the ratio $D_e/D$ to the $\lambda$-value and the ratio of the diameters of the diffusing species and the effective resin pore diameter.

In Chapter 6 the activities of various strong acid ion exchange resins for the hydration of alkenes are compared using the hydration of 2-methylpropene as test reaction. Experiments to determine the reaction rate constant of the hydration reaction have been performed at atmospheric pressure and temperatures in the range 10 - 60°C. On the basis of a comparison of the rates of the hydration reaction catalyzed by strong acid resins and by homogeneous aqueous solutions of strong acids, an effective value of the Hammett acidity function ($H^*$) can be ascribed to each resin ($H_{0,r}$), which can also be used to predict the catalytic activity of the resin for the hydration of other alkenes. $H_{0,r}$ values for a number of commercially available strong acid ion exchange resins are in the range -0.7 to -1.0, corresponding with nitric acid solutions of 2.1 to 3 M. The $H_{0,r}$ value becomes more negative with increasing crosslinking percentage, indicating that the catalytic activity increases with crosslinking percentage.
On the basis of experiments on the rate of hydration of 2-methylpropene, the Wheeler-Thiele theory has been found suitable to describe (internal) diffusion limited reactions in ion exchange particles.

Chapter 7 describes the thermal deactivation in water of several strong acid resins in the H⁺-form. Experiments have been performed in a fixed-bed flow reactor at temperatures between about 155 and 205°C. The deactivation is caused by the removal of sulfonic acid groups from the polymer matrix, giving sulfuric acid. The removal of sulfonic acid groups is found to be catalyzed by hydrogen ions, which in the present case originate from the acid groups in the resin. The thermal stability seems to increase with decreasing crosslinking percentage of the resin, indicating that the influence of the crosslinking on the catalytic activity of the resin for its own decomposition is qualitatively similar to that for the hydration reaction.

Two types of -SO₃H groups are present in the resins, showing widely differing rates of decomposition. The reaction by which the more stable -SO₃H groups (about 90% of the initial capacity) decompose, has an activation energy of approximately 120 kJ·mol⁻¹ for most resins tested. At the highest temperatures in the range studied the resin type XE-307, which probably contains chlorinated styrene units, is the most stable one.

In Chapter 8 some of the consequences of the results described in the previous chapters for the design of an industrial butene hydration reactor are discussed. The hydration of a butene-rich C₄ mixture is preferably carried out in a packed bed reactor, at temperatures in the range 130 - 140°C and at pressures slightly above the saturation pressure of the butenes. The butene-rich phase is preferably fed to the bottom of a packed bed reactor, in which the water-rich phase is the continuous one. Product 2-butanol is removed from the reactor at the top with the butene-rich phase. The conversion per pass is limited to about 15%, caused by chemical equilibrium and mass-transfer limitations. Therefore a large butene recycle is required, necessitating the use of high purity butene feeds. Feed mixtures high in 1-butene content show the highest 2-butanol production rates. Reactor volumes required for a 2-butanol production rate of 50,000 t/a are 100 - 200 m³, depending on the process conditions.

To overcome the rather severe chemical equilibrium limitations and mass transfer resistances the addition of an inert solvent for both water and the butenes seems promising.