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DIMERISATION OF ISOBUTENE ON ACIDIC ION-EXCHANGE RESINS

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Abstract

Dimerisation of isobutene produces diisobutenes that can be hydrogenated to isooctane (2,2,4-trimethyl pentane). Isooctane can be used as a high octane gasoline component. The aim of this work was to study the selective production of diisobutenes through the dimerisation of isobutene on ion-exchange resin catalysts and to construct kinetic models for the reactions in the system for reactor design purposes.

High selectivities for diisobutenes were obtained in the presence of polar components such as methanol and *tert*-butyl alcohol (TBA). The effects of these polar components were found to be basically the same, i.e. the selectivity for diisobutenes increases with the content of the polar component while the activity of the catalyst decreases. Because TBA does not react with isobutene and because small amounts are sufficient to obtain high selectivities, TBA was concluded to be a good selectivity-enhancing component and was used in further studies of the system.

Different ion-exchange resin structures in the dimerisation of isobutene were studied and it was observed that good accessibility to the active sites gives high isobutene conversions and medium crosslinking high selectivities for diisobutenes. When linear butenes were added to the feed of the system, they were found to react with isobutene to codimers especially at low TBA contents and at high temperatures. In these experiments some 2-butanol was formed from the linear butenes and the water from TBA dehydration.

In the kinetic modelling, it was observed that a basic Langmuir–Hinshelwood-type kinetic model describes the diisobutene formation rates well. Similar model was constructed for the codimerisation of isobutene and 2-butenes. The trimerisation of isobutene was found to proceed via diisobutenes and an additional free catalyst active site participates in the reaction. TBA dehydration was well described by Langmuir–Hinshelwood-type kinetics where the formed isobutene does not adsorb on the catalyst and only one active site is needed. In the simulation of miniplant-scale reactors these models were found to represent the experimental data well and thus they can be used in reactor design.

Preface

The work for this thesis was carried out at the Helsinki University of Technology in the laboratory of Industrial Chemistry between May 2001 and December 2004. Funding was received from Neste Oil Oyj (former Fortum Oil Oy) and from the Academy of Finland through the Graduate School in Chemical Engineering (GSCE). Foundation of Technology (TES) provided a personal grant.

I wish to express my warmest thanks to my supervisor, Professor Outi Krause for her continuous support and valuable discussions and comments during my studies. Many thanks to my co-authors Tuomas Ouni, Dr. Marina Lindblad and Prof. Juhani Aittamaa for valuable discussions and for Dr. Andrew Root for performing the NMR measurements. I also wish to thank the project members for co-operation and especially Dr. Kari Keskinen for his helpful comments.

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Finally, warm thanks to the two most important people in my life: thank you, Antti, for all your help and patience and thank you, Miia, for filling my days with laughter and joy.

Espoo, October 2005,

Maija Honkela

List of publications

This thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals (Appendices I–VI):

- I M. L. Honkela and A. O. I. Krause, Influence of polar components in the dimerization of isobutene, *Catal. Lett.* **87** (2003) 113–119.
- II Maija L. Honkela, Andrew Root, Marina Lindblad and A. Outi I. Krause, Comparison of ion-exchange resin catalysts in the dimerisation of isobutene, *Appl. Catal. A* **295** (2005) 216–223.
- III Maija L. Honkela and A. Outi I. Krause, Kinetic modeling of the dimerization of isobutene, *Ind. Eng. Chem. Res.* **43** (2004) 3251–3260.
- IV Maija L. Honkela and A. Outi I. Krause, Influence of linear butenes in the dimerization of isobutene, *Ind. Eng. Chem. Res.* **44** (2005) 5291–5297.
- V Maija L. Honkela, Tuomas Ouni and A. Outi I. Krause, Thermodynamics and kinetics of the dehydration of *tert*-butyl alcohol, *Ind. Eng. Chem. Res.* **43** (2004) 4060–4065.
- VI Tuomas Ouni, Maija Honkela, Aspi Kolah and Juhani Aittamaa, Isobutene dimerisation in a miniplant-scale reactor, accepted for publication in *Chem. Eng. Process.*

Maija Honkela's contribution to the appended publications:

- I She participated in the planning and performing of the methanol and MTBE experiments and in the interpretation of the results. She wrote the manuscript.
- II She planned the sodium exchange experiments, interpreted the results and wrote the manuscript together with the co-authors.
- III She carried out part of the experiments and the kinetic analyses. She interpreted the results and wrote the manuscript.
- IV She participated in the planning of the experiments, carried out the kinetic analyses and wrote the manuscript.
- V She planned and performed the experiments and carried out the thermodynamic and kinetic analyses. She wrote the manuscript together with the co-authors.
- VI She provided the kinetic models for the simulations and participated in the interpretation of the results.

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Chapter 1

Introduction

Gasoline for fuel engines needs to be of high octane number. This number describes the knocking resistance of the gasoline and, by definition, isooctane (2,2,4-trimethyl pentane) has octane number 100 and n-heptane 0. Lead components were once added to gasoline to increase the octane number, but in the 1980s, when they became recognised as environmentally harmful, they were gradually replaced by various ethers. Methyl *tert*-butyl ether (MTBE) was one of these ethers.

MTBE has a high blending octane number (RON/MON=118/100 [1]) and as an oxygen-containing compound it promotes clean burning of fuel. Generally it is produced from isobutene (iB) and methanol (MeOH) under mild reaction conditions (below 100 °C) on ion-exchange resin catalysts. Dimethyl ether and diisobutenes (diB) are produced in the main side reactions of the process [2].

Although MTBE is an excellent gasoline component, one property has caused problems: its water solubility is 4.3 wt-% [3] and it has occasionally found its way into ground water from leaking storage tanks. Although MTBE has not been found carcinogenic in studies of its health effects [4], its foul taste and smell have caused it to be banned in California [5,6].

In addition to finding new octane-enhancing components for gasoline, new uses need to be found for the isobutene feedstocks formerly used in the MTBE production. Both problems can be solved by producing high-octane components insoluble in water by the dimerisation of isobutene. In the dimerisation diisobutenes, i.e. 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (RON/MON=100/89 [7]) are formed. Diisobutenes can be used as such to replace MTBE in gasoline, or, if alkene limitations are exceeded, they can be hydrogenated to isooctane. Hydrogenation can be carried out for example with a nickel catalyst below 100 °C [8]. Another approach is diisobutene etherification with various alcohols [9, 10] as a means of producing good gasoline components.

1.1 Characteristics of the isobutene dimerisation

In an oil refinery isobutene for the dimerisation process is available from fluid catalytic cracking (FCC), steam cracking (SC) and isobutane dehydrogenation. The butenes from FCC are washed with sodium hydroxide solutions and thus traces of sodium hydroxide may enter the isobutene dimerisation process and deactivate the catalyst. Feeds from FCC and SC include also linear butenes that may react with isobutene to codimers [7, 11].

In the ion-exchange resin catalysed isobutene etherification low alcohol-to-alkene molar feed ratios have been shown to favour isobutene dimerisation [2, 12, 13]. Under ether synthesis conditions without the alcohol, however, higher oligomers are formed in addition to diisobutenes [7]. Adding even small amounts of polar components noticeably increases the selectivity for diisobutenes.

Polar components in the feed increase the selectivity for diisobutenes, but also decrease the activity of the resin. This results in easier control of the process, because isobutene dimerisation and oligomerisation reactions are highly exothermic [14]. Reliable kinetic models are important in the design and optimisation of the process.

1.2 Commercial technologies for the production of diisobutenes

Many of the currently available commercial technologies for the production of diisobutenes or isooctane employ alcohols to obtain diisobutenes selectively. These technologies are presented in Table 1.1 together with the catalyst and additive type used in the isobutene dimerisation. The most common additives are methanol, which reacts with isobutene to MTBE, and *tert*-butyl alcohol (TBA), which does not form an ether with isobutene [15] but dehydrates to water and isobutene.

Table 1.1: Commercial technologies for the production of diisobutenes.

Ref.	Company	Technology	Catalyst	Additive
[16]	Neste Oil and Kellogg Brown & Root	NExOCTANE	acid resin	water/TBA
[17]	CDTECH and Snamprogetti	CDIsoether	acid resin	water/TBA or MeOH/MTBE
[18]	UOP	InAlk	SPA* or acid resin	water/TBA
[19]	IFP	Dimersol	nickel	-
[20]	Lyondell	Alkylate 100	acid resin	water/TBA

* solid phosphoric acid

Most of the technologies use acidic ion-exchange resin catalysts. Only IFP's Dimer-sol process [19] converts linear butenes selectively to diisobutenes on a nickel catalyst dissolved in ionic liquid. Products of this process are easily separated because they are poorly soluble in the ionic solvent. In UOP's InAlk process, solid phosphoric acid (SPA) catalyst can be used instead of an acidic resin [18]. Water is then added to control the conversion and the selectivity.

Usually TBA or water is added to increase the selectivity for diisobutenes with acidic ion-exchange resin catalysts. Exceptionally, in the *CDIsoether* technology

developed by Snamprogetti and Catalytic Distillation Technologies (CDTECH), methanol may be used [17] in addition to TBA. Then isobutene can be partially dimerised and partially etherified, as desired. Pure TBA or water is used in the NExOCTANETM process developed by Neste Oil and Kellogg Brown & Root [16], in UOP's InAlk process [18] and in the Alkylate 100 process by Lyondell [20]. Diisobutenes are thus produced free of MTBE and in high yield.

1.3 Aim of this work

Even though several commercial technologies exist for the dimerisation of isobutene, the scientific understanding of the reaction is limited. Furthermore, detailed kinetic models are important in the optimisation of this challenging process. The purpose of this thesis was to thoroughly study the selective production of diisobutenes via the ion-exchange resin catalysed dimerisation of isobutene and to construct kinetic models for the reactions in the system.

Isobutene dimerisation experiments carried out without polar components resulted in very low diisobutene selectivities. Because both methanol and TBA are used to enhance the selectivity in commercial processes, paper I compared the effects of these two polar components. Because TBA performed better, it was used as the selectivity enhancing component in further studies.

Various ion-exchange resins and resins ion-exchanged with sodium were tested as catalysts in the dimerisation of isobutene to study the effect of catalyst properties on catalyst performance in the system [II]. In paper III kinetic rate equation for the isobutene dimerisation in the presence of TBA was proposed. The kinetics of three side reactions (trimerisation of isobutene [III], the codimerisation of isobutene and 2-butenes (2B) [IV] and the dehydration of TBA [V]) were studied to supplement the kinetic knowledge on the system. In paper VI some of the kinetic models were used in the simulation of miniplant-scale reactors to test their ability to represent the system.

Chapter 2

Experimental

2.1 CSTR reactor system

Isobutene dimerisation experiments were carried out in a continuous stirred tank reactor (CSTR, 50 cm³) operating in liquid phase. Two feeding tanks were used, one containing the alkene feed as a liquid, and the other a mixture of the polar component and the solvent (isopentane, iP). The feeding tanks were pressurised with nitrogen to 1.8 MPa. The flow through the reactor was achieved with a pressure difference as the pressure in the reactor was kept at 1.5 MPa. The reactor was heated with hot oil flowing through the reactor jacket.

At the beginning of each experiment the alkene, isopentane and additive flow was analysed by gas chromatography. After the flow had stabilised and had been accurately analysed, it was fed to the reactor. The flow from the reactor was analysed and the reaction at each temperature was allowed to continue until a steady state was reached. The temperature was then changed. An automation system was used to gather measured data and to control the reactor temperature.

The flows to and from the reactor were analysed with an on-line Hewlett-Packard 5890 Series II gas chromatograph, which was equipped with an HP-1 capillary column (length 60 m, film thickness 1.00 μm and diameter 0.25 mm) and a flame ionisation detector. The products were quantified by an internal standard method. Water could not be measured with the used detector and thus TBA dehydration was studied based on the TBA balance.

2.2 Batch reactor system

TBA dehydration experiments were carried out in a stainless steel batch reactor (80 cm^3). The catalyst was placed in the reactor in a metal gauze basket. The reactor was pressurised with nitrogen to about 1.3 MPa to keep the reaction mixture in liquid phase. The reactor was held in a thermostated water bath with which various temperatures could be maintained. Samples were taken manually through a sample valve.

The samples were analysed off-line with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a DB-1 capillary column (length 60 m, film thickness 1.00 μm and diameter 0.25 mm) and a flame ionisation detector. Products were quantified by an internal standard method and the amounts of water and isobutene were calculated from the TBA molar balance.

2.3 Chemicals

The alkenes studied were isobutene (Aga, 99%) 1-butene (1B, Aga, 99%), *cis*-2-butene (c-2B, Aga, 99%) and a isobutene-*cis*-2-butene mixture (49.5 wt-% iB and 49.4 wt-% c-2B). TBA (MERCK-Schuchardt, >99%; Riedel-de Haën, $\geq 99.5\%$), methanol (Riedel-de Haën, >99.8%), MTBE (supplied by Neste Oil, >95%) and

2-butanol (2-BuOH, Riedel-de Haën, $\geq 99\%$) were used as additives. Isopentane (Fluka Chemika AG, $\geq 99\%$) was used as a solvent and isooctane (Fluka Chemika AG, $\geq 99.5\%$) was added to the reaction mixture in the batch experiments to study the reliability of the sampling.

2.4 Catalysts

The catalyst in the study of the polar components [I] and in the kinetic studies [III-V] was a commercial ion-exchange resin that consisted of a styrenedivinylbenzene-based support to which sulphonic acid groups had been added as active sites. Before use the catalyst was dried overnight in an oven at about 100 °C.

In the catalyst comparison study [II] several ion-exchange resins by Rohm & Haas were tested in the dimerisation of isobutene with the CSTR equipment. These resins included surface sulphonated XE586, highly crosslinked (divinylbenzene (DVB) content 85% [21]) XN1010, monosulphonated A15 and A16 and corresponding hypersulphonated A35 and A36 and gel-type (8 DVB-% [22]) A39. Details of these resins are given in paper II. Ion-exchange resin A15 treated with sodium hydroxide solutions to acid capacities of 3.9, 3.1 and 2.1–2.3 mmol_{H+} g⁻¹ was also tested in the system [II].

2.5 Experiments

The components in the feed, the catalyst and the reactor system in the experiments that have been carried out for papers I-V are summarised in Table 2.1. The details of the miniplant-scale reactor experiments are presented in paper VI.

In the CSTR experiments the total mass flow was about 36 g h⁻¹ and the amount of dry catalyst 1 g. The molar feed ratios (alkene/(solvent+additive)) were between

Table 2.1: Performed experiments.

Ref.	Alkene	Additive	Catalyst	Reactor system
I	iB	-	basic*	CSTR
	”	MeOH	”	”
	”	TBA	”	”
	”	MTBE	”	”
II	iB	TBA	various resins	CSTR
	”	”	NaOH treated	”
III	iB	TBA	basic*	CSTR
IV	1B	TBA	basic*	CSTR
	c-2B	”	”	”
	c-2B	2-BuOH	”	”
	iB	”	”	”
	iB+c-2B	TBA	”	”
V	-	TBA	basic*	batch

* a commercial acidic ion-exchange resin

0.6 and 1.1, the additive contents 0–18 mol-% and the temperatures 60–120 °C.

In separate TBA dehydration experiments [V] the reaction conditions were chosen so that the isobutene that was formed would not react further to diisobutenes, and thus dehydration equilibrium and kinetics could be studied in the absence of the dimerisation of isobutene. These batch reactor experiments were carried out with TBA contents 2–18 mol-% at temperatures 60–90 °C.

2.6 Reaction products

Diisobutenes and triisobutenes were the main products of the isobutene dimerisation experiments. Tetramer content was less than 2 mol-% even without TBA.

The main diisobutenes were 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene, the ratio of which was very close to the thermodynamic equilibrium obtained by Karinen et al. [23]. In the kinetic modelling, all the diisobutenes were considered as one pseudocomponent, and all the triisobutenes as another.

In addition to dimerisation and oligomerisation reactions, MTBE formation from methanol and isobutene occurred in the experiments with methanol [I]. TBA dehydration to water and isobutene was observed in the isobutene dimerisation experiments at higher temperatures [III]. In the experiments with the isobutene-*cis*-2-butene mixture, isobutene and 2-butenes formed codimers [IV].

Chapter 3

Effect of reaction conditions

3.1 Polar components

Isobutene dimerisation in the absence of polar components [I] gave very low diisobutene selectivity (24% at 80 °C) as was expected from the studies of Di Girolamo et al. [7] and Scharfe [11]. Although the selectivity was this low in the steady state, diisobutenes were the main products in the beginning of the experiment before the steady state was reached. This suggests that triisobutenes form in a consecutive reaction via diisobutenes.

Further experiments were carried out with both TBA and methanol to study the effect of polar components on the selectivity [I]. The results showed that the conversion decreases and the selectivity increases with the increasing content of the polar component. Conversion increased with temperature in the TBA experiments, but temperature had no clear effect in the methanol experiments. In later studies the conversion was observed to increase with the isobutene-to-solvent molar feed ratio, while the selectivity decreased [III].

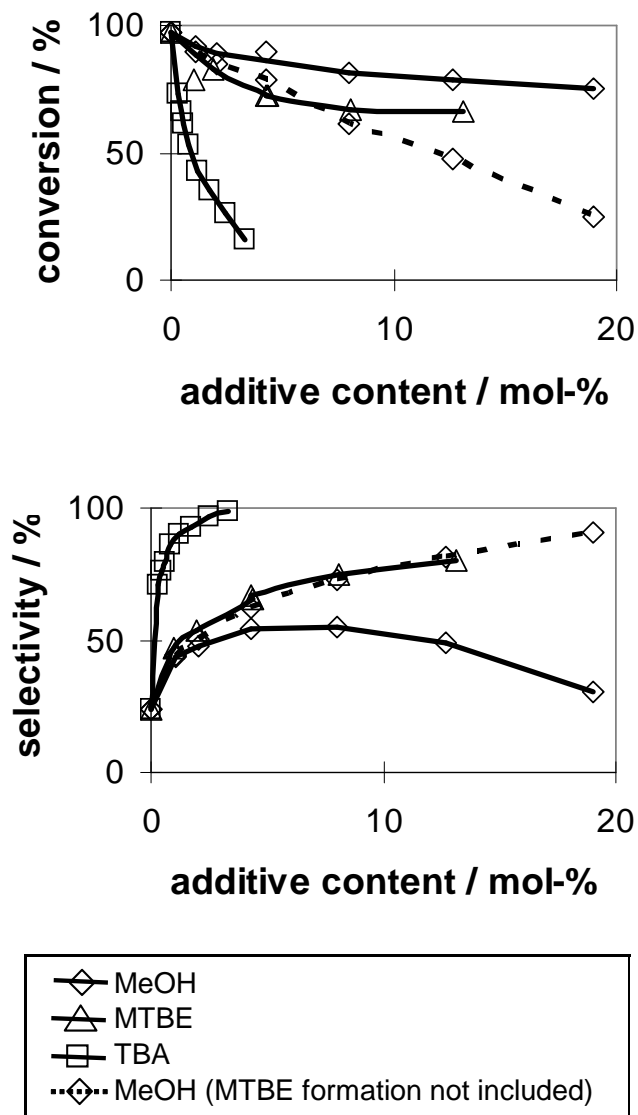


Figure 3.1: Isobutene conversion and diisobutene selectivity with the various additives. The dotted curve for methanol shows the conversion and selectivity in the methanol experiments when MTBE formation is not included in the calculations [I].

MTBE was used as an additive in some experiments so that the extent and the effect of the MTBE formation in the methanol experiments could be assessed. Figure 3.1 shows that the total isobutene conversion is lower and the selectivity for diisobutenes higher with MTBE than with methanol. This is understandable, because in the methanol experiments isobutene is consumed in the MTBE formation. When the conversion of isobutene to oligomers and the selectivity for diisobutenes were calculated without MTBE formation, the values for the methanol and MTBE experiments were the same. Methanol was observed to react almost entirely to MTBE and thus MTBE, not methanol, is present on the catalyst in the methanol experiments and increases the selectivity for diisobutenes.

Comparison of the various polar components is shown in Figure 3.2. The results of the experiments with 2-butanol in the feed (paper IV) have been included in the figure, too. The additives give the same selectivity with the same conversion level, which suggests that their effects are in principle the same. The only difference is in the amount needed for the same results and thus in the strength of the effect.

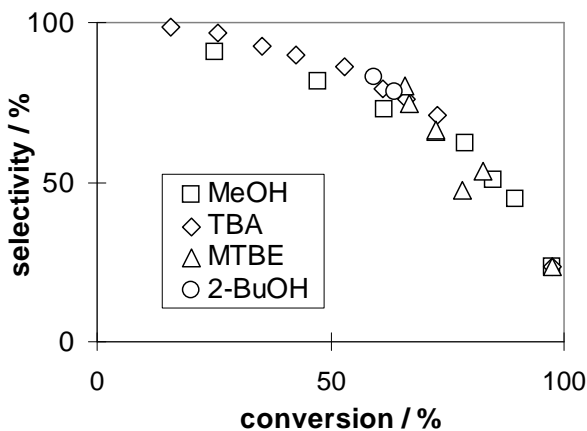


Figure 3.2: Selectivity for diisobutenes as a function of the isobutene conversion in the experiments with the various additives at 80 °C [I,IV].

The differences between the effects of the various polar components can be explained by their different polarity. Comparison of the properties of TBA and MTBE shows that TBA has a higher dielectric constant (for TBA at 30 °C 10.9 [24] and for MTBE at 20 °C 2.6 [25]), and thus is more polar than MTBE. Higher polarities suggest higher concentrations on the catalyst, which is why less TBA is needed to increase the selectivity for diisobutenes. Much more MTBE is required to achieve the same conversion and selectivity.

The effect of polar components in the dimerisation of isobutene was also studied by Di Girolamo and Marchionna [26]. They compared the results of experiments with methanol, ethanol and isopropanol (alcohol/isobutene molar ratio 0.2) and isopropanol, sec-butanol and TBA (alcohol/isobutene molar ratio 0.05). Their results showed that the conversion is lower and the selectivity higher with higher alcohols such as ethanol than with methanol. This is because the etherification does not proceed as far with ethanol as with methanol and thus more ethanol stays on the catalyst and decreases the activity. Since TBA does not form an ether but rather dehydrates to water, which adsorbs more strongly on the catalyst than any of the alcohols, its effect is the strongest. The study of Di Girolamo and Marchionna was made by comparing the results with constant alcohol to isobutene ratio and thus it does not show the similarity of the effects of the alcohols that we observed.

The results obtained with the sodium hydroxide treated resins were used to study whether the increase in the selectivity can be obtained by reducing the activity of the resin by deactivating part of the active sites [II]. The selectivity for diisobutenes as a function of the isobutene conversion in these experiments is presented in Figure 3.3. The TBA contents were 0.5, 1.0 and 2.0 mol-%. Different selectivities with the same conversion level are obtained with the resins deactivated to various capacities. It was also noticed that the selectivities decrease with the decreasing acid capacity. This means that the activity decrease does not result in increased selectivity in these experiments, and the influence of the sodium ions and of the polar components on the catalyst is different.

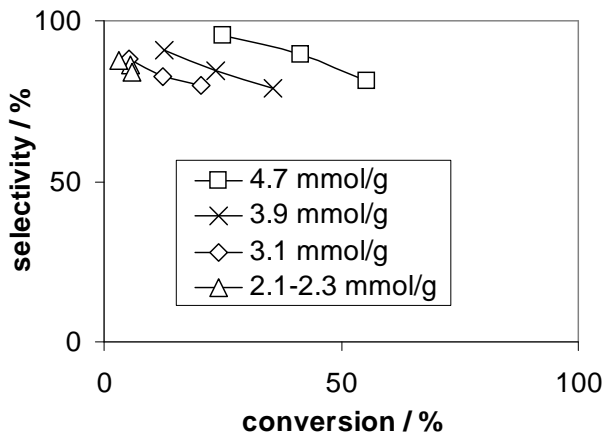


Figure 3.3: Selectivity for diisobutenes as a function of the isobutene conversion in the experiments with the sodium hydroxide treated resins at 80 °C (TBA contents 0.5, 1.0 and 2.0 mol-%) [II].

The acidities of the active sites change when additives such as polar components or sodium ions are in contact with the resin. The relative average acidities of the acid groups of the resins were measured by ^{13}C cross-polarisation magic angle spinning (CP-MAS) NMR [II]. These measurements showed that TBA and ion-exchanged sodium decrease the acidity of the acid groups similarly. This means that although in the dimerisation of isobutene the influence of TBA and of the sodium ions on the selectivity for diisobutenes is different, their influence on the acidity of the resin is similar. Different interaction with the protons of the catalyst is a possible explanation for their different behaviour in the isobutene dimerisation experiments. The polar components are strong proton acceptors, and may participate in the chain scission by claiming the proton of the intermediate carbonium ion [27]. Sodium ions, on the other hand, adsorb strongly on the acid sites and also decrease the swelling of the catalyst [28]. Thus they hinder the mobility of the protons and of the products. These diffusion problems give the components more time to react to higher oligomers and thus result in decreased selectivity.

Results presented in Paper I show that polar components increase the selectivity for diisobutenes in the dimerisation of isobutene. When in contact with the resin, polar components decrease the activity of the resin which results in increased selectivity. Furthermore, because activity decrease caused by sodium ions gives low selectivities [II], polar components may assist in the chain scission also separately and not only through the activity decrease. TBA is a good selectivity-enhancing component, because it does not form ethers with isobutene and small amounts give high selectivities for diisobutenes.

3.2 Catalyst structure

The polymer supports of the ion-exchange resins used in this study were built of polystyrene chains linked with divinylbenzene (DVB). These components form a macroporous structure which can be described to consist of gel-type microspheres [29]. The DVB content determines the surface area and the pore size distribution of the resin [30], and also specifies the rigidity of the structure and the extent of swelling in the presence of a polar component.

In this study the polymer support had a charge caused by SO_3^- groups. This charge was neutralised with positive labile and exchangeable H^+ ions. In nonpolar conditions the sulphonic acid sites function as active sites, but with high water (or alcohol) contents the reactions proceed on the less active solvated protons [31,32]. The sulphonic acid sites are situated on the easily accessible macropores, but also inside the gel-type microspheres [33].

The dependence of the isobutene dimerisation rates on the acid capacity were studied with the sodium hydroxide treated ion-exchange resin A15. The conversion was found to decrease with the increasing sodium content and fitting the rate data with the acid concentration gave the average reaction order of 2.3. The isobutene dimerisation was concluded to be a second order reaction with respect to the acid

capacity and in the comparison of the catalysts the diisobutene formation rates were calculated based on the square of the acid capacity.

Catalysts A15, A16, A35, A36 and A39 had similar acid capacities (4.7–5.4 mmol_{H+} g⁻¹ [34]) and thus they could be compared based on the mass of the catalyst. The results showed that there are only minor differences between the activities of these resins.

Ion-exchange resins XE586 and XN1010 had acid capacities 1.3 mmol_{H+} g⁻¹ [35] and 3.3 mmol_{H+} g⁻¹ [36], respectively. In the experiments the TBA contents (2 mol-%) and the amounts of catalyst (1 g of dry catalyst) were the same independent of the acid capacity of the catalyst. Thus there are differences in the TBA contents relative to the acid capacities, and because XE586 and XN1010 had lower acid capacities than the other resins, they had even higher TBA contents relative to the acid capacity. The selectivities as a function of the conversion for XE586, XN1010, A35 and A36 at 90 °C are presented in Figure 3.4. With catalysts A35 and A36 similar selectivities as a function of the conversion are obtained as observed with various polar components in Figure 3.2. With the different polar components the same selectivities were obtained with the same conversion levels when the amount of the polar component and thus the content of the polar component relative to the acid capacity was changed (section 3.1). Now XE586 and XN1010 give lower selectivities with the same conversion levels as the other catalysts, which suggests that their different behaviour does not only result from their different TBA to acid capacity ratios.

XE586 and XN1010 showed clearly higher diisobutene formation rates based on the square of the acid capacity than the other resins. Ion-exchange resin XE586 is surface sulphonated and XN1010 has high crosslinking degree (85 DVB-% [21]) and thus most of the active sites on the surface of the macropores. With these two catalysts the high activity based on the acid capacity can be explained by the good accessibility of the acid sites.

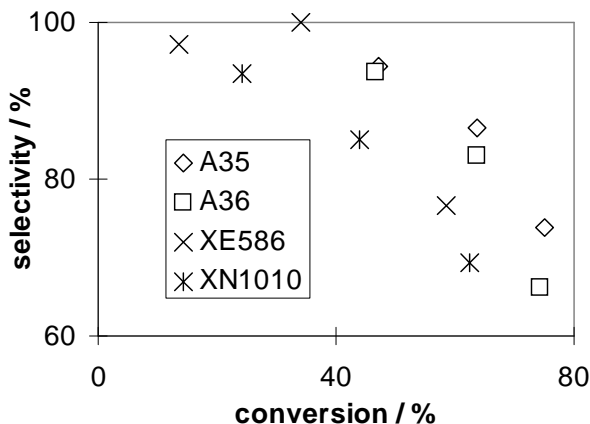


Figure 3.4: The selectivities for diisobutenes as a function of the isobutene conversion in experiments with A35, A36, XE586 and XN1010 as catalysts at 90 °C [II].

The best diisobutene selectivities as a function of the temperature were obtained with the surface sulphonated ion-exchange resin XE586, while at 110 °C both XN1010 and A39 displayed lower selectivities than the other resins. XN1010 has high crosslinking degree, A39 low (8 DVB-% [22]) and the other resins medium crosslinking (12–20 DVB-% [21]). With XE586 fast diffusion from the active surface prevents oligomerisation and results in good selectivity for diisobutenes. XN1010 has higher surface area and crosslinking and thus more rigid structure and smaller pores than XE586. A39, on the other hand, has low crosslinking degree which is why it requires a polar solvent to swell and allow good accessibility to the active sites. This low TBA contents (2 mol-%) are perhaps not sufficient for it to function properly. Similarly as with the sodium exchanged resins (section 3.1) the compact structures of XN1010 and A39 hinder the positive effect of TBA.

The results suggest that it is beneficial to have the active sites near the surface, because this increases the accessibility of the sites and decreases diffusion problems. The catalyst structure, however, should not be too rigid nor too flexible, because medium crosslinking gives the best selectivities.

3.3 Linear butenes

Linear butenes are present in the feed for the isobutene dimerisation system especially if it is from fluid catalytic cracking or steam cracking [7, 11]. Earlier studies have shown that 1-butene and 2-butenes in these feeds increase the selectivity for dimers, because they adsorb on the active sites more preferably than the dimers [7]. Further experiments were now carried out with linear butenes to study their reactivity under the isobutene dimerisation conditions with TBA present.

The experiments with the linear butenes showed that their dimerisation is slow under the studied conditions. The isomerisation of 1-butene to cis- and trans-2-butenes was fast, while cis-2-butene isomerised to trans-2-butene but hardly at all to 1-butene. Previously Słomkiewicz [37], too, observed that the isomerisation rates of 2-butenes to 1-butene are low and when Nierlich et al. [38] studied the oligomerisation of 2-butenes, they observed that the product composition did not change when 2-butenes were partly replaced by 1-butene. The isomerisation reactions did not reach thermodynamic equilibria [39, 40] in our experiments and the reaction rates decreased considerably at high TBA contents.

In the experiments with the mixture of isobutene and cis-2-butene, cis-2-butene isomerised to trans-2-butene. 2-Butenes were more reactive when isobutene was present than when pure 2-butene feed was used. Codimers were formed from isobutene and 2-butenes. Figure 3.5 shows that the fraction of diisobutenes from the formed dimers increased with the increasing TBA content and decreasing temperature. Naturally the conversion of 2-butenes follows the opposite trend and their reactivity increases with the decreasing TBA content and increasing temperature.

In the experiments with the pure linear butenes TBA dehydrated almost completely and the formed water reacted with the linear butenes to 2-butanol. All the linear butenes give the same *sec*-butyl carbonium ion which may react with

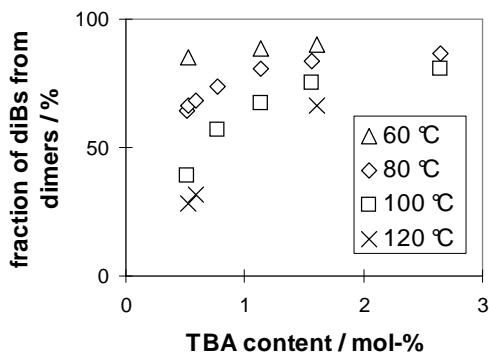


Figure 3.5: Fraction of diisobutenes from dimers as a function of the TBA content in the feed in the experiments with the isobutene-*cis*-2-butene mixture feed.

water to 2-butanol [41]. Also in the experiments with the mixture of isobutene and *cis*-2-butene part of the TBA dehydrated and formed 2-butanol. 2-Butanol has similar effect on the selectivities as TBA as shown in Figure 3.2, but may form ethers with alkenes.

In the absence of polar components 1-butene in the feed to the isobutene dimerisation system has been found to decrease the conversion of isobutene and to increase the total selectivity for C₈ dimers [42] and in the presence of methanol linear butenes have been found to increase the selectivity for C₈ dimers [7]. Now in the presence of TBA its effect on the conversion of isobutene is significant and introducing 2-butenes to the feed of the system hardly affects the conversion. Also the selectivity for C₈ dimers remains unaffected.

Based on the results it can be concluded that the reactivities of the pure linear butenes under the isobutene dimerisation conditions are low. The rate of isomerisation of linear butenes and the rate of codimerisation of isobutene and 2-butenes depend on the amount of TBA. Furthermore, water from the dehydration of TBA reacts partly with the linear butenes to corresponding alcohols.

Chapter 4

Kinetics

On the basis of paper I, TBA could be considered a good selectivity-enhancing component. The isobutene dimerisation system with TBA was accordingly studied further, to obtain kinetic equations for the reactions.

Experiments were carried out to study if internal or external mass transfer limitations existed, but no limitations were observed [III,V]. No catalyst deactivation was observed in any of the experiments.

Dortmund modified UNIFAC method [43,44] was used to calculate the activities in the kinetic and thermodynamic analyses that were carried out with Kinfit software [45]. In the modelling of the data the sum of squares of the residuals between the measured and calculated inlet compositions (mol h^{-1} , CSTR, [III, IV]) or the measured and calculated compositions (mol , batch, [V]) was minimised.

4.1 Isobutene dimerisation and trimerisation

Several earlier studies on isobutene dimerisation kinetics exist and most of them consider the dimerisation as a side reaction of ether production. It has been suggested that the reaction order changes with isobutene concentration [46], and Eley–Rideal-type reaction [2, 47] has been proposed. Haag [47] found that the triisobutenes form through both consecutive and parallel reactions, i.e. via diisobutenes and directly from isobutene. Tetramer formation was confirmed to proceed only after all isobutene had been converted. In these previous studies, isobutene dimerisation has mostly been studied in the absence of polar components and thus these models cannot be used to describe an isobutene dimerisation system where the selectivity for diisobutenes is increased with a polar component.

The measured data for the kinetic study in paper III showed some interesting features. The rate of diisobutene formation reached a maximum at about 1 mol-% TBA content. Furthermore, the triisobutene formation rate decreased rapidly with increasing TBA content. TBA dehydration occurred at higher temperatures (100 and 120 °C), but even then the conversion to water was less than 30%. Because TBA is the only source of water, the amounts of TBA and water are correlated. Furthermore, the amount of isobutene formed from TBA is small. TBA dehydration was not, therefore, included in the kinetic models in paper III, but rather a new series of experiments were carried in the absence of isobutene in a batch reactor, and the results are presented in paper V.

Although previous publications suggest Eley–Rideal-type isobutene dimerisation under certain conditions, the present data do not support this kind of mechanism. These earlier studies were carried out in the absence of polar components and thus it is possible that polar components change the order of the isobutene dimerisation reaction, as was suggested by Hauge [42]. Langmuir–Hinshelwood-type reaction equations were now derived for both the dimerisation and the trimerisation of isobutene. The formation of triisobutenes both directly from isobutenes and via

diisobutenes was considered, as well as the number of active sites needed in the reaction.

Although TBA dehydration was not included in the kinetic models, the effect of the polar components (TBA and water) was taken into account in the rate equations for isobutene dimerisation and trimerisation. The effect of the polar components was simplified to result from their adsorption on the active sites of the catalyst. The adsorption decreases the amount of free active sites resulting in decreased conversion. The amount of TBA in the feed was used as the combined amount of TBA and water in the reactor.

In deriving the isobutene dimerisation and trimerisation models it was assumed that the amount of unoccupied active sites on the catalyst is small and that the surface reaction is the rate-limiting step. Adsorption of the solvent on the catalyst was found to be significant and it was included in the models. Best representation of the measured data was obtained with a model where triisobutenes are formed via diisobutenes, as was also expected based on the experiments in paper I. Furthermore, because of the maximum in the diisobutene formation rate as a function of the TBA content, three active sites are needed in the trimerisation of isobutene. The net reaction rates for a system where the diisobutene formation proceeds through two adsorbed isobutenes on separate active sites and the triisobutene formation through adsorbed diisobutene, adsorbed isobutene and an additional free active site are

$$r_{iB} = -2 \cdot \frac{k_{diB} a_{iB}^2}{(a_{iB} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP})^2} - \frac{k_{triB} a_{iB} a_{diB}}{(a_{iB} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP})^3} \quad (4.1)$$

$$r_{diB} = \frac{k_{diB} a_{iB}^2}{(a_{iB} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP})^2} - \frac{k_{triB} a_{iB} a_{diB}}{(a_{iB} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP})^3} \quad (4.2)$$

$$r_{triB} = \frac{k_{triB} a_{iB} a_{diB}}{(a_{iB} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP})^3}, \quad (4.3)$$

where

$$k_{diB} = F_{diB} \exp \left[-\frac{E_{diB}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right],$$

$$k_{triB} = F_{triB} \exp \left[-\frac{E_{triB}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$$

and $T_{\text{ref}} = 373.15$ K. This type of model explains the maximum in the diisobutene rate and the strong decrease in the triisobutene rate at low TBA contents.

The optimised parameters for the isobutene dimerisation and trimerisation models are presented in Table 4.1. The parameters are well identified and only the activation energy for the isobutene trimerisation has a wide confidence limit (1.8 ± 15.1 kJ mol⁻¹).

Table 4.1: Values of the parameters and their 95% confidence limits for the isobutene dimerisation and trimerisation models.

Parameter	Value
F_{diB} , mol/(h g _{cat})	0.82 ± 0.42
E_{diB} , kJ/mol	30 ± 3
F_{triB} , mol/(h g _{cat})	0.065 ± 0.052
E_{triB} , kJ/mol	1.8 ± 15.1
$K_{\text{TBA}}/K_{\text{iB}}$	7.0 ± 2.4
$K_{\text{iP}}/K_{\text{iB}}$	0.12 ± 0.06

Measured di- and triisobutene formation rates and those calculated with Equations (4.1)–(4.3) and the parameters presented in Table 4.1 at 100 °C with the molar feed ratio 0.6 are shown in Figure 4.1. The calculated rates describe the data well; only at higher TBA contents there is a small deviation between the calculated and measured diisobutene formation rates. Figure 10 in paper III shows also some deviations at low reaction rates (low temperatures and/or high TBA contents).

Based on the kinetic study it seems that the effects of the polar components in the dimerisation of isobutene can be expressed by their adsorption on the active sites. The isobutene dimerisation is quite well described by basic Langmuir–Hinshelwood-type kinetics, while the isobutene trimerisation requires an additional free active site.

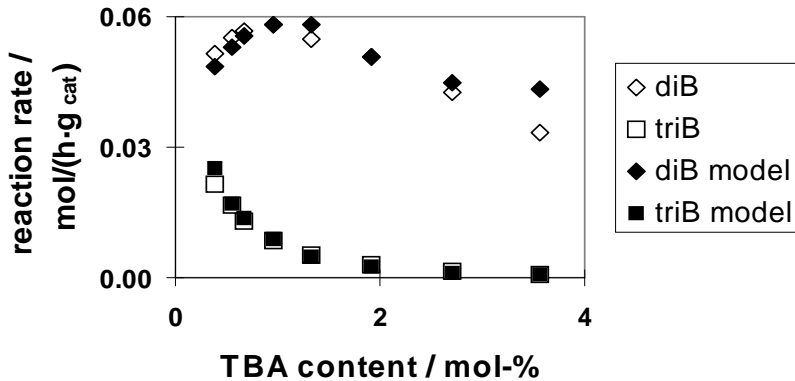


Figure 4.1: Measured and calculated di- and triisobutene formation rates at 100 °C with the molar feed ratio (IB/(IP+TBA)) 0.6.

4.2 Codimerisation of isobutene and 2-butenes

In paper IV the rate equation for the codimerisation of isobutene and 2-butenes was added to the previously presented isobutene dimerisation model. In addition to the assumptions presented in Section 4.1, it was assumed that 2-butenes are consumed only in the codimerisation and codimers (dim) do not react further to trimers. These additional assumptions were made because the experimental data showed that the 2-butene dimerisation was slow with pure *cis*-2-butene feed and about the same amount of trimer peaks were obtained with the isobutene–*cis*-2-butene mixture as with pure isobutene at 60 and 80 °C. The amount of TBA in the feed was used as the combined amount of TBA, water, 2-butanol and ether in the reactor.

Reaction rate equations were derived for the dimerisation of isobutene, codimerisation of isobutene and 2-butenes and the trimerisation of isobutene through di-

isobutenes. The net reaction rate equations for the system are:

$$r_{iB} = -2 \cdot r_{diB,j} - r_{dim,j} - r_{triB,j} \quad (4.4)$$

$$r_{2B} = -r_{dim,j} \quad (4.5)$$

$$r_{diB} = r_{diB,j} - r_{triB,j} \quad (4.6)$$

$$r_{dim} = r_{dim,j} \quad (4.7)$$

$$r_{triB} = r_{triB,j} \quad (4.8)$$

where

$$r_{diB,j} = \frac{k_{diB} a_{iB}^2}{\left(a_{iB} + \frac{K_{2B}}{K_{iB}} a_{2B} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP}\right)^2},$$

$$r_{dim,j} = \frac{k_{dim} a_{iB} a_{2B}}{\left(a_{iB} + \frac{K_{2B}}{K_{iB}} a_{2B} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP}\right)^2},$$

$$r_{triB,j} = \frac{k_{triB} a_{iB} a_{diB}}{\left(a_{iB} + \frac{K_{2B}}{K_{iB}} a_{2B} + \frac{K_{TBA}}{K_{iB}} a_{TBA} + \frac{K_{iP}}{K_{iB}} a_{iP}\right)^3}$$

and

$$k_{diB} = F_{diB} \exp \left[-\frac{E_{diB}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right],$$

$$k_{dim} = F_{dim} \exp \left[-\frac{E_{dim}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right],$$

$$k_{triB} = F_{triB} \exp \left[-\frac{E_{triB}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right].$$

The equations now include also the adsorption of 2-butenes. The data in the study of the isobutene dimerisation kinetics [III] and the data obtained with the mixture of isobutene and *cis*-2-butene [IV] was used to optimise the parameters of this model. The optimised parameters are presented in Table 4.2. The parameters that were optimised in Section 4.1 for isobutene dimerisation and trimerisation and were presented in Table 4.1 agree well with the parameters in Table 4.2 and have now even better confidence limits.

Based on the results it seems that with the assumptions made an adequate presentation of an isobutene dimerisation system with 2-butenes and TBA present can be obtained.

Table 4.2: Values of the parameters and their 95% confidence limits for the rate equations of the isobutene dimerisation system with 2-butenes present described in equations (4.4)–(4.8).

Parameter	Value
F_{diB} , mol/(h g _{cat})	0.70 ± 0.28
E_{diB} , kJ/mol	30 ± 2
F_{dim} , mol/(h g _{cat})	0.14 ± 0.07
E_{dim} , kJ/mol	29 ± 13
F_{triB} , mol/(h g _{cat})	0.053 ± 0.033
E_{triB} , kJ/mol	1.4 ± 12.6
$K_{\text{TBA}}/K_{\text{iB}}$	6.3 ± 1.8
$K_{\text{iP}}/K_{\text{iB}}$	0.11 ± 0.04
$K_{\text{2B}}/K_{\text{iB}}$	0.071 ± 0.059

4.3 TBA dehydration

The dehydration of TBA is an equilibrium-limited endothermic reaction and thus more water is produced at higher temperatures. Because water is more polar than TBA, it may have a significant effect on the diisobutene selectivities. In the isobutene dimerisation experiments reported in paper III, water production was negligible, but in industrial scale it is probable that the dehydration of TBA has a more important role.

Several studies describe TBA dehydration and its reverse reaction isobutene hydration. The main difference in these two type of studies is the initial amount of water, because in the isobutene hydration the catalyst is often fully swollen [48,49]. Both reactions have been modelled to proceed through carbonium ions [49,50], and Langmuir–Hinshelwood-type kinetics have been reported [31].

TBA dehydration experiments were now [V] carried out in the batch reactor under conditions similar to isobutene dimerisation until it was certain that equilibrium had been reached. Although the reaction is relatively fast and almost complete during the first hour, at least six hours was allowed for the whole system to reach equilibrium on an initially dry catalyst.

Temperature-dependent reaction equilibrium constants and reaction enthalpies and entropies were calculated from the obtained equilibrium data. The values were found to agree well with the values reported in the literature. For example, the reaction enthalpy here was $26 \pm 9 \text{ kJ mol}^{-1}$, while reported values range between 26.5 and 39 kJ mol^{-1} [49, 51, 52].

Assumptions made in deriving the kinetic models for the dehydration of TBA were similar to those made in the modelling of the isobutene dimerisation and trimerisation data in paper III. Although the three tested TBA dehydration models resulted in very similar fits, the most reliable parameters were obtained with a Langmuir–Hinshelwood-type model where the formed isobutene does not adsorb on the catalyst. The reaction rates for this type of system are

$$-r_{\text{TBA}} = \frac{F_{\text{TBA}} \exp\left(-\frac{E_{\text{TBA}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref},2}}\right)\right)(K_a a_{\text{TBA}} - a_{\text{H}_2\text{O}} a_{\text{iB}})}{a_{\text{TBA}} + \frac{K_{\text{H}_2\text{O}}}{K_{\text{TBA}}} a_{\text{H}_2\text{O}}}, \quad (4.9)$$

$$r_{\text{iB}} = r_{\text{H}_2\text{O}} = -r_{\text{TBA}}, \quad (4.10)$$

where K_a is the temperature-dependent reaction equilibrium constant

$$K_a = \exp\left(-3111.9 \frac{1}{T/\text{K}} + 7.6391\right) \quad (4.11)$$

determined from the data and $T_{\text{ref},2} = 343.15 \text{ K}$. One basic difference when compared with the isobutene dimerisation model is that, in the TBA dehydration the solvent was found not to adsorb on the catalyst, whereas in the dimerisation of isobutene its adsorption could not be neglected.

The optimised parameters for the TBA dehydration model are presented in Table 4.3. The measured and calculated molar fractions as a function of time at 60 °C

Table 4.3: Values of parameters and their confidence limits for the TBA dehydration model.

Parameter	Value
F_{TBA} , mol/(h g _{cat})	0.74 ± 0.37
E_{TBA} , kJ/mol	18 ± 6
$K_{\text{H}_2\text{O}}/K_{\text{TBA}}$	1.5 ± 1.1

for the TBA dehydration model are presented in Figure 4.2. The figure shows that the model represents the data well.

This model was not used to describe TBA dehydration in the modelling of the isobutene dimerisation data in paper III, because the water contents in the CSTR product flow remained low. Both dimerisation and TBA dehydration models were used in the simulation of miniplant-scale reactors, the results of which are discussed in Section 4.5.

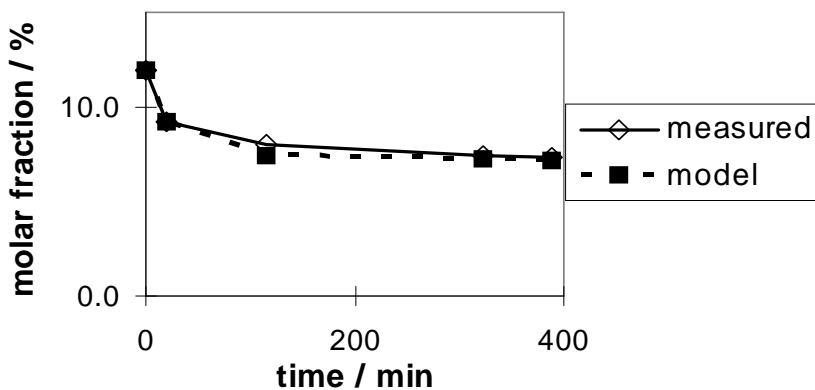


Figure 4.2: Measured and calculated molar fractions of TBA as a function of time in the dehydration of TBA at 60 °C.

4.4 Parameter values

In the rate equations for isobutene dimerisation and trimerisation the adsorption equilibrium constants for di- and triisobutenes were found to be much smaller than the adsorption equilibrium constant for isobutene ($K_{\text{diB}}/K_{\text{iB}} = 74 \cdot 10^{-6}$, $K_{\text{triB}}/K_{\text{iB}} = 21 \cdot 10^{-3}$ [III]). Smaller values for the adsorption of diisobutenes than isobutene were also found by Haag [47]. In contrast to this, Izquierdo et al. [46] obtained higher adsorption equilibrium constants for diisobutenes than for isobutene for their semiempirical Langmuir–Hinshelwood and Eley–Rideal-type model combination. The adsorption equilibrium constants of Haag [47] and Izquierdo et al. [46] are presented in Table 4.4. The models of Haag and Izquierdo et al. did not include polar components.

Table 4.4: Adsorption equilibrium parameters from the literature.

Ref.	Catalyst	T/K	K_{iB}	K_{diB}
Haag [47]	Amberlyst 15	293.15	≥ 40 l/mol	3.5 l/mol
Izquierdo et al. [46]	Lewatit K-2631	323.15	0.27 l/mol	0.59 l/mol
		333.15	0.031 l/mol	0.22 l/mol

The adsorption equilibrium constants obtained for the rate equations follow the order $K_{2\text{B}} < K_{\text{iP}} < K_{\text{iB}} < K_{\text{TBA}} < K_{\text{H}_2\text{O}}$. This seems reasonable since the most polar components adsorb on the catalyst the most strongly [53]. The smaller adsorption equilibrium constant for 2-butenes than for isopentane is still exceptional, because alkenes should adsorb on the catalyst more than alkanes [53]. Furthermore, because the solvent has a clear effect in the isobutene dimerisation, but can be omitted in the TBA dehydration kinetics, it is possible that the adsorption equilibrium constant for isopentane represents some other solvent effect in the system than merely the adsorption of isopentane on the catalyst.

In the TBA dehydration model adsorption equilibrium constant of water relative to that of TBA was 1.5 ± 1.1 . This means that the extent of adsorption of both water and TBA on the catalyst is of the same order of magnitude. In the isobutene dimerisation model water was not included in the model separately, but both TBA and water contents in the outlet of the reactor were represented by the TBA content in the inlet. Adsorption equilibrium constants of the same order of magnitude for TBA and water give credibility to this assumption.

The activation energy for the isobutene dimerisation is low ($30 \pm 3 \text{ kJ mol}^{-1}$), but in agreement with previous studies where activation energies between 40 and 50 kJ mol^{-1} were obtained for similar systems [54–57]. This low values suggest that there may be some diffusion problems in the gel-phase as has been suggested by Rehfinger and Hoffmann [54] and Hauge [42, 57].

Activation energy for codimerisation ($29 \pm 13 \text{ kJ mol}^{-1}$) was of the same order of magnitude as the activation energy for isobutene dimerisation. Activation energies for the isobutene trimerisation were not found in the literature for comparison. The activation energy is correlated with the other parameters and its value is very small ($1.8 \pm 15.1 \text{ kJ mol}^{-1}$).

Activation energies between 67 and 69 kJ mol^{-1} have been found for the isobutene hydration on ion-exchange resin Amberlyst 15 [58, 59]. The activation energy obtained here for the TBA dehydration is $18 \pm 6 \text{ kJ mol}^{-1}$, which is quite low especially when the obtained reaction enthalpy was $26 \pm 9 \text{ kJ mol}^{-1}$. Also here gel-phase diffusion problems might explain the low activation energy.

4.5 Simulation of miniplant-scale reactors

The isobutene dimerisation and trimerisation models [III] and the TBA dehydration model [V] were used in the simulation of experiments carried out in a

miniplant-scale reactor [VI]. Miniplant-scale systems are used in the process development between laboratory and bench scale equipment, the objective being the reduction of testing stages in the scale-up.

The reactor system now consisted of two tubular reactors (diameters 16 mm) in series. The length of the catalyst bed in the first reactor was 0.431 m and in the second 0.592 m and the catalyst was partly predried before use. The average flow rate applied was 280 g h^{-1} . The feed and product compositions were analysed by gas chromatography. Diisobutene yields up to 59% were obtained corresponding to the isobutene conversion of 63% and diisobutene selectivity of 98% (TBA content 2.5 wt-% and temperature $75 \text{ }^\circ\text{C}$).

For the simulation of the experiments, a 2-dimensional tubular reactor model was constructed. This model included also the kinetic rate equations presented in papers III and V. The simulation of the experiments with the derived model gave good correspondence to the isobutene conversions and diisobutene selectivities obtained in the experiments, and also the maximum temperature in the reactor was well predicted. Some deviations between the simulated and measured TBA conversions were observed possibly because water and TBA had not reached proper steady state in the experiments.

The successful simulation of a different reactor system and independent experimental results confirms that the obtained kinetic models can be applied in the process development.

Chapter 5

Conclusions

In this work the selective production of diisobutenes through the dimerisation of isobutene was studied. Experiments were carried out on ion-exchange resin catalysts in the presence of polar components that increase the selectivity for diisobutenes.

The effects of two selectivity-enhancing components, methanol and TBA, were compared. Methanol was found to react almost entirely to MTBE on the catalyst and thus MTBE was the selectivity-enhancing component in the methanol experiments. The effects of the two components were found to be basically the same, but more MTBE than TBA was needed to reach good selectivity because of its lower polarity. TBA does not form ethers with isobutene, and high selectivities are achieved even when its content in the feed is low. In view of this, TBA was selected for use in further studies.

Deactivation of part of the acid groups of an ion-exchange resin by sodium was found to decrease the activity of the resin similarly as the polar components. Still, the selectivities for diisobutenes were also decreased. Sodium was deduced

to decrease the mobility of the active protons and the diffusion of the produced components. The polar components, on the other hand, may help in the chain scission because of their strong proton accepting character.

When various ion-exchange resins were tested as catalysts in the dimerisation of isobutene, good accessibility of the active sites and thus high level of surface sulphonation was found to give high activity. Medium crosslinking (12–20 DVB-%) gave the best selectivities.

Dimerisation of pure linear butenes under the isobutene dimerisation conditions was found to be slow while the isomerisation proceeded faster. When a mixture of isobutene and 2-butenes was used as a feed, codimers were formed in addition to diisobutenes. The codimerisation rate decreased clearly at low temperatures and high TBA contents. It was further noticed that some water from the dehydration of TBA reacted with the linear butenes to 2-butanol that increases the selectivity similarly as TBA.

Kinetic equations were derived for the dimerisation of isobutene and three important side reactions, i.e. the trimerisation of isobutene, the codimerisation of isobutene and 2-butenes and the dehydration of TBA. For the isobutene dimerisation and trimerisation the kinetic analysis gave Langmuir–Hinshelwood-type rate equations where the effect of TBA was well described by its adsorption on the active sites of the resin. Similar rate equation was obtained for the codimerisation of isobutene and 2-butenes. TBA dehydration kinetics were studied in separate experiments and the equilibrium data obtained agreed well with those reported in the literature. The best kinetic model was a Langmuir–Hinshelwood-type model where only one active site participates in the reaction.

The obtained kinetic rate equations for the isobutene dimerisation and trimerisation and the TBA dehydration were used in the simulation of miniplant-scale reactors. The successful simulation confirms that the kinetic models can be used in reactor design.

Abbreviations, IUPAC names and notation

a_i	activity of component i
1B	1-butene
2B	2-butenes
2-BuOH	2-butanol
<i>c</i> -2B	<i>cis</i> -2-butene
CP-MAS	cross-polarisation magic angle spinning
CSTR	continuous stirred tank reactor
diB	diisobutenes, 2,4,4-trimethyl pentenes
dim	C ₈ dimers other than diisobutenes
DVB	divinylbenzene
E	activation energy, kJ mol ⁻¹
F	preexponential factor, mol h ⁻¹ g _{cat} ⁻¹
FCC	fluid catalytic cracking
iB	isobutene, 2-methyl propene
iP	isopentane, 2-methyl butane
isooctane	2,2,4-trimethyl pentane
k	reaction rate constant, mol h ⁻¹ g _{cat} ⁻¹
K_a	reaction equilibrium constant based on activities
K_i	adsorption equilibrium constant of component i

MeOH	methanol
MON	motor octane number
MTBE	methyl <i>tert</i> -butyl ether, 2-methoxy-2-methyl propane
R	universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
r_i	reaction rate of component i , $\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$
RON	research octane number
SC	steam cracking
SPA	solid phosphoric acid
t-2B	<i>trans</i> -2-butene
T	temperature, K
T_{ref}	reference temperature, K
TBA	<i>tert</i> -butyl alcohol, 2-methyl-2-propanol
tetraB	tetraisobutenes, tetramers
triB	triisobutenes, trimers

Bibliography

- [1] Unzelman, G. H., Oxygenates for the future – 1. U.S. clean air act expands role for oxygenates, *Oil Gas J.* **89** (15) (1991) 44–48.
- [2] Vila, M., Cunill, F., Izquierdo, J.-F., González, J. and Hernández, A., The role of by-products formation in methyl *tert*-butyl ether synthesis catalyzed by a macroporous acidic resin, *Appl. Catal. A* **117** (1994) L99–L108.
- [3] Piel, W. J., Diversify future fuel needs with ethers, *Fuel Reformulation* **4** (2) (1994) 28–33.
- [4] Anon., US scientists vote against fuel additive ban, *Chem. Ind.* (1) (1999) 4.
- [5] Executive order D-5-99 by the Governor of the State of California, 25 March 1999.
- [6] Executive order D-52-02 by the Governor of the State of California, 15 March 2002.
- [7] Di Girolamo, M., Lami, M., Marchionna, M., Pescarollo, E., Tagliabue, L. and Ancillotti, F., Liquid-phase etherification/dimerization of isobutene over sulfonic acid resins, *Ind. Eng. Chem. Res.* **36** (1997) 4452–4458.
- [8] Lylykangas, M. S., Rautanen, P. A. and Krause, A. O. I., Liquid-phase hydrogenation kinetics of isooctenes on Ni/Al₂O₃, *AIChE J.* **49** (2003) 1508–1515.
- [9] Karinen, R. S. and Krause, A. O. I., Reactivity of some C₈-alkenes in etherification with methanol, *Appl. Catal. A* **188** (1999) 247–256.

- [10] Karinen, R. S., Linnekoski, J. A. and Krause, A. O. I., Etherification of C₅- and C₈-alkenes with C₁- to C₄-alcohols, *Catal. Lett.* **76** (2001) 81–87.
- [11] Scharfe, G., Convert butenes to high octane oligomers, *Hydrocarbon process.* **53** (4) (1973) 171–173.
- [12] Tejero, J., Calderón, A., Cunill, F., Izquierdo, J. F. and Iborra, M., The formation of byproducts in the reaction of synthesis of isopropyl *tert*-butyl ether from isopropyl alcohol and isobutene on an acidic macroporous copolymer, *React. Funct. Polym.* **33** (1997) 201–209.
- [13] Linnekoski, J. A., Krause, A. O. I., Holmen, A., Kjetså, M. and Moljord, K., Etherification of isobutene with 1-propanol and 2-propanol, *Appl. Catal. A* **174** (1998) 1–11.
- [14] Alcántara, R., Alcántara, E., Canoira, L., Franco, M. J., Herrera, M. and Navarro, A., Trimerization of isobutene over Amberlyst-15 catalyst, *React. Funct. Polym.* **45** (2000) 19–27.
- [15] Macho, V., Kavala, M., Polievka, M., Okresa, M. and Piecka, W., Production of alkyl *tert*-butyl ethers, *Ropa Uhlie* **24** (1982) 397–409.
- [16] Hunszinger, P., Järvelin, H., Puroola, V.-M., Nurminen, M., Khalil, M. S. and Birkhoff, R., Start-up and operation of the first on-purpose iso-octane unit at Alberta Envirofuels Inc., Edmonton, Canada, *NPRA 2003 Annual Meeting*, San Antonio, Texas, March 23–25, 2003, AM-03-43.
- [17] Sahay, N., McGuirk, T., Marchionna, M. and Tagliabue, L., Low cost conversion of MTBE units to alternative gasoline blending components production, *NPRA 2002 Annual Meeting*, San Antonio, Texas, March 17–19, 2002, AM-02-18.
- [18] UOP, Fuels for the 21st century. URL http://www.uop.com/solutions_and_innovation/Issues%20%26%20Solutions/MakingPremiumAlkylate.pdf, (accessed Nov 2003).

- [19] Chauvin, Y., Olivier, H., Wyrvalski, C. N., Simon, L. C. and de Souza, R. F., Oligomerization of n-butenes catalyzed by nickel complexes dissolved in organochloroaluminate ionic liquids, *J. Catal.* **165** (1997) 275–278.
- [20] Anon., Lyondell chemical company - licensed technologies. URL <http://www.lyondell.com/html/products/Licensing/olefins.shtml#alkylate>, (accessed Dec 2004).
- [21] Lange, J.-P. and Petrus, L., Solid acid catalysts for converting alkenes and alkanols to carboxylic acids, *Appl. Catal. A* **216** (2001) 285–294.
- [22] Liu, W.-T. and Tan, C.-S., Liquid-phase esterification of propionic acid with n-butanol, *Ind. Eng. Chem. Res.* **40** (2001) 3281–3286.
- [23] Karinen, R. S., Lylykangas, M. S. and Krause, A. O. I., Reaction equilibrium in the isomerization of 2,4,4-trimethyl pentenes, *Ind. Eng. Chem. Res.* **40** (2001) 1011–1015.
- [24] Weast, R. C. and Astle, M. J., Eds., *CRC Handbook of Chemistry and Physics*, 63. Ed., CRC Press, USA 1984, pp. E-51, E-52.
- [25] Anon., ARCOPURE High Purity MTBE. URL <http://www.lyondell.com/html/products/techlit/2601.pdf>, (accessed Apr 2005).
- [26] Di Girolamo, M. and Marchionna, M., Acidic and basic ion exchange resins for industrial applications, *J. Mol. Catal. A: Chem.* **177** (2001) 33–40.
- [27] Roberts, J. D. and Caserio, M. C., *Modern Organic Chemistry*, W. A. Benjamin Inc., New York 1967.
- [28] Dorfner, K., Ed., *Ion Exchangers*, Walter de Gruyter, Berlin, New York 1991.
- [29] Chakrabarti, A. and Sharma, M. M., Cationic ion exchange resins as catalyst, *React. Polym.* **20** (1993) 1–45.
- [30] Jacobelli, H., Bartholin, M. and Guyot, A., Styrene divinyl benzene copolymers. I. Texture of macroporous copolymers with ethyl-2-hexanoic acid in diluent, *J. Appl. Polym. Sci.* **23** (1979) 927–939.

- [31] Gates, B. C. and Rodriguez, W., General and specific acid catalysis in sulfonic acid resin, *J. Catal.* **31** (1973) 27–31.
- [32] Thornton, R. and Gates, B. C., Catalysis by matrix-bound sulfonic acid groups: Olefin and paraffin formation from butyl alcohols, *J. Catal.* **34** (1974) 275–287.
- [33] Jeřábek, K., The effect of inhomogeneity of the polymer structure on catalytic activity of ion exchangers, *Collect. Czech. Chem. Commun.* **44** (1979) 2612–2618.
- [34] Web pages of Rohm and Haas Co., Amberlyst strong acid cations. URL <http://www.rohmmaas.com/ionexchange/IP/sac.htm>, (accessed Dec 2004).
- [35] Pääkkönen, P. K. and Krause, A. O. I., Comparative study of TAME synthesis on ion-exchange resin beads and a fibrous ion-exchange catalyst, *React. Funct. Polym.* **55** (2003) 139–150.
- [36] Marchionna, M., Di Girolamo, M. and Patrini, R., Light olefins dimerization to high quality gasoline components, *Catal. Today* **65** (2001) 397–403.
- [37] Słomkiewicz, P. M., Isomerization of C-4 alkenes catalysed by macroporous ion exchange resin, *React. Funct. Polym.* **33** (1997) 299–304.
- [38] Nierlich, F., Neumeister, J. and Wildt, T., The oligomerization of lower olefins by heterogenous catalysis, *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **36** (1991) 585–595.
- [39] Golden, D. M., Egger, K. W. and Benson, S. W., Iodine-catalyzed isomerization of olefins. I. Thermodynamic data from equilibrium studies of positional and geometrical isomerization of 1-butene and 2-butene, *J. Am. Chem. Soc.* **86** (1964) 5416–5420.
- [40] Meyer, E. F. and Stroz, D. G., Thermodynamics of n-butene isomerization, *J. Am. Chem. Soc.* **94** (1972) 6344–6347.

- [41] Petrus, L., De Roo, R. W., Stamhuis, E. J. and Joosten, G. E. H., Kinetics and equilibria of the hydration of linear butenes over a strong acid ion-exchange resin as catalyst, *Chem. Eng. Sci.* **41** (1986) 217–226.
- [42] Hauge, K., *Oligomerization of isobutene over solid acid catalysts for production of high octane gasoline*, Doctoral thesis, Norwegian University of Science and Technology, Trondheim, 2004.
- [43] Weidlich, U. and Gmehling, J., A modified UNIFAC model. 1. Prediction of VLE, h^E and γ^∞ , *Ind. Eng. Chem. Res.* **26** (1987) 1372–1381.
- [44] Lohmann, J., Joh, R. and Gmehling, J., From UNIFAC to modified UNIFAC (Dortmund), *Ind. Eng. Chem. Res.* **40** (2001) 957–964.
- [45] Aittamaa, J. and Keskinen, K. I., *Kimfit*, Laboratory of Chemical Engineering, Helsinki University of Technology, Espoo, Finland, 2001.
- [46] Izquierdo, J. F., Vila, M., Tejero, J., Cunill, F. and Iborra, M., Kinetic study of isobutene dimerization catalyzed by a macroporous sulphonic acid resin, *Appl. Catal. A* **106** (1993) 155–165.
- [47] Haag, W. O., Oligomerization of isobutylene on cation exchange resins, *Chem. Eng. Progr. Symp. Ser.* **63** (1967) 140–147.
- [48] Gupta, V. P. and Douglas, W. J. M., Diffusion and chemical reaction in isobutylene hydration within cation exchange resin, *AIChE J.* **13** (1967) 883–889.
- [49] Velo, E., Puigjaner, L. and Recasens, F., Inhibition by product in the liquid-phase hydration of isobutene to *tert*-butyl alcohol: Kinetics and equilibrium studies, *Ind. Eng. Chem. Res.* **27** (1988) 2224–2231.
- [50] Gates, B. C., Wisnouskas, J. S. and Heath Jr., H. W., The dehydration of *t*-butyl alcohol catalyzed by sulfonic acid resin, *J. Catal.* **24** (1972) 320–327.
- [51] Delion, A., Torck, B. and Hellin, M., Equilibrium constant for the liquid-phase hydration of isobutylene over ion-exchange resin, *Ind. Eng. Chem. Process Des. Dev.* **25** (1986) 889–893.

- [52] Iborra, M., Tejero, J., El-Fassi, M. B., Cunill, F., Izquierdo, J. F. and Fité, C., Experimental study of the liquid-phase simultaneous syntheses of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA), *Ind. Eng. Chem. Res.* **41** (2002) 5359–5365.
- [53] Helfferich, F., *Ion Exchange*, McGraw-Hill Book Co., New York 1962.
- [54] Rehfinger, A. and Hoffmann, U., Formation of di-isobutene, main by-product of methyl tertiary butyl ether synthesis catalyzed by ion exchange resin, *Chem. Eng. Technol.* **13** (1990) 150–156.
- [55] Kogelbauer, A., Nikolopoulos, A. A., Goodwin, J. G. and Marcelin, G., Reactant adsorption and its impact upon methyl MTBE synthesis on zeolites, *J. Catal.* **152** (1995) 122–129.
- [56] Shah, N. F. and Sharma, M. M., Dimerization of isoamylene: Ion exchange resin and acid-treated clay as catalysts, *React. Polym.* **19** (1993) 181–190.
- [57] Hauge, K., Oligomerization of isobutene over solid acid catalysts, *Catal. Today* **100** (2005) 463–466.
- [58] Zhang, C. M., Adesina, A. A. and Wainwright, M. S., Isobutene hydration over Amberlyst-15 in a slurry reactor, *Chem. Eng. Process.* **42** (2003) 985–991.
- [59] Leung, P., Zorrilla, C., Recasens, F. and Smith, J. M., Hydration of isobutene in liquid-full and trickle-bed reactors, *AIChE J.* **32** (1986) 1839–1847.