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Heterogeneously Catalyzed Saucy-Marbet Ketonization Reactions

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presented by

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Summary

In industrial fine chemical syntheses, chain elongation reactions play an important role. Condensation reactions of unsaturated alcohols and unsaturated ethers to form unsaturated ketones are key steps in synthesis of intermediate products in flavour, fragrance, vitamin and fine chemical syntheses. These ketonization reactions, first investigated by G. Saucy and R. Marbet, are normally carried out with homogeneous acid catalysts, which are often difficult to separate from product mixtures and are environmentally harmful. Therefore, economically unfavourable recycling processes are necessary.

In this work, solid acids were explored as catalysts for two different ketonization reactions. These insoluble solid acids provide the advantage of facile separation from the product stream (by filtering) and relatively easy handling. Experiments were carried out in a continuous flow laboratory scale reactor and in an autoclave.

Ketonization of dehydrolinalool to form 6,10-dimethyl-4,5,9-undecatrien-2-one, an intermediate product in synthesis of pseudoionone (an important compound in vitamin E and K production), was first investigated. A catalyst screening of several different acid catalysts was carried out to select the most efficient catalyst. Deloxan ASP I/9, an alkyl sulfonic acid polysiloxane, proved to be the most suitable catalyst for this ketonization reaction. Catalytic experiments concerning time on stream behaviour and parametric sensitivity were carried out in the continuous flow system. Yields of the desired product, related to dehydrolinalool, of up to 54 % could be achieved.

These promising results led to the idea to broaden the application range of heterogeneous acid catalysts by testing another reactant for this Saucy-Marbet ketonization reaction. 2-methyl-3-butyn-2-ol was chosen as an unsaturated alcohol with shorter chain length and thus a lower molecular weight and a boi-

ling point closer to that of the co-reactant, the vinyl ether (2-methoxypropene). Deloxan ASP I/9 again served as catalyst to investigate time on stream behaviour and parametric sensitivities in the continuous flow reactor system. With this reactant, yields of the desired product (6-methyl-4,5-heptadien-2-one), related to fed 2-methyl-3-butyn-2-ol, of up to 45 % were reached.

When Deloxan ASP I/9 was used as catalyst, in both ketonization reactions, selectivities of more than 80 % could be observed, whereas conversions of the unsaturated alcohols were never higher than 60 %.

To compare ketonization reactions in conventional solvent (toluene) with the same reactions in "supercritical" carbon dioxide ("scCO$_2$"), which showed improved mixing conditions in other reactions, and with solventless processing, experiments in a batch reactor system were carried out. Ketonization of 2-methyl-3-butyn-2-ol in "scCO$_2$" afforded less than half of the yield achieved in toluene, but dehydrolinalool-ketonization with the "supercritical" solvent gave yields of the desired product, related to dehydrolinalool, that were about three times as high as with toluene. Nevertheless, compared to the solventless reaction, application of "scCO$_2$" as solvent for DLL-ketonization did not bring an improvement in performance.

The interaction of 2-methoxypropene with heterogeneous acid catalysts containing sulfonic acid groups covalently bound to SiO$_2$ and sulfuric acid adsorbed on TiO$_2$-modified amorphous SiO$_2$, respectively, was investigated by *in situ* attenuated total reflection infrared spectroscopy. Rapid hydrolysis is observed, which does however not require the acid sites. The resulting acetone is adsorbed predominantly on SiOH groups. Promoted by the acid sites a further transformation is observed on the catalyst. Based on the time behaviour of the ATR signals of acetone and the product the further reaction likely involves the condensation of 2-methoxypropene and acetone. During the build up of the reaction product hydronium ions disappear from the catalyst surface. Upon desorption of the reaction product the hydronium ions reappear to a large extent on the catalyst containing adsorbed sulfuric acid, whereas they reappear to a lesser degree on the catalyst, which contains sulfonic acid groups. The two investigated acid catalysts contain vastly different relative concentrations of Brønsted and Lewis sites, which can explain the difference in the relative con-

centration of intermediate and product at the interface in the observed consecutive reaction.

The combined kinetic and spectroscopic studies indicate that application of solid acids in the Saucy-Marbet ketonization reaction is an attractive alternative to conventional homogeneous catalysts that are used in fine chemical syntheses. Although similarly high yields as achieved with homogeneous catalysts could not be reached, heterogeneous catalysts have the advantage of facile separation from product stream and thus lead probably to simpler product cleaning processes. The results show the potential of a continuous process using a heterogeneous catalyst, though the achievement of this goal requires further effort.

Zusammenfassung

In industriellen feinchemischen Synthesen spielen Kettenverlängerungs-Reaktionen eine wichtige Rolle. Kondensationsreaktionen von ungesättigten Alkoholen und ungesättigten Ethern, zur Bildung von ungesättigten Ketonen, sind wichtige Schritte in der Synthese von Zwischenprodukten für die Herstellung von Aromen, Duftstoffen, Vitaminen und Feinchemikalien. Diese Ketonisierungsreaktionen, die als erste von G. Saucy und R. Marbet untersucht worden sind, werden normalerweise mit homogenen sauren Katalysatoren durchgeführt, die häufig schwierig von den Produktgemischen zu trennen und zudem umweltschädigend sind. Folglich sind aufwändige Aufarbeitungsprozesse notwendig.

In dieser Arbeit wurden feste Säuren als Katalysatoren für zwei unterschiedliche Ketonisierungsreaktionen verwendet. Diese unlöslichen festen Säuren haben den Vorteil der einfachen Trennung vom Produktstrom (durch Abfiltrierung) und relativ problemloser Handhabung. Experimente wurden in einem kontinuierlich betriebenen Labormassstab Reaktor-System und in einem Autoklaven durchgeführt.

Die Ketonisierung von Dehydrolinalool, um 6,10-Dimethyl-4,5,9-undecatrien-2-on, ein Zwischenprodukt in der Synthese von Pseudoionon (eine wichtige Komponente in der Vitamin E- und K-Produktion), zu synthetisieren, wurde an erster Stelle untersucht. Ein Katalysator-Screening einiger unterschiedlicher saurer Katalysatoren wurde durchgeführt, um danach den leistungsfähigsten Katalysator auszuwählen. Deloxan ASP I/9, ein Alkylsulfonsäure Polysiloxan, war der aussichtsreichste Katalysator zum Einsatz in dieser Ketonisierungsreaktion. Die katalytischen Experimente im Hinblick auf Erkenntnisse des zeitlichen Verhaltens und der Parameter-Empfindlichkeit wurden im kontinuierlich betriebenen Reaktor-System durchgeführt. Ausbeu-

ten des gewünschten Produkts, in Bezug auf eingesetztes Dehydrolinalool, von bis zu 54 % konnten erzielt werden.

Diese vielversprechenden Resultate führten zur Idee, das Anwendungsgebiet der heterogenen sauren Katalysatoren zu erweitern, indem ein anderes Substrat in dieser Saucy-Marbet Ketonisierungsreaktion verwendet wurde. 2-Methyl-3-butyn-2-ol, ein ungesättigter Alkohol mit einer kürzeren Kettenlänge und folglich einem tieferen Molekulargewicht und einem Siedepunkt im Bereich desjenigen des Vinylethers (2-Methoxypropen), wurde für weitere Experimente gewählt. Deloxan ASP I/9 diente erneut als Katalysator, um das zeitliche Verhalten der Katalyse und die Parameter-Empfindlichkeit im kontinuierlich betriebenen Reaktor-System zu untersuchen. Mit diesem Substrat wurden Ausbeuten des gewünschten Produktes (6-Methyl-4,5-heptadien-2-on), relativ zum ins System gepumpten 2-Methyl-3-butyn-2-ol, von bis zu 45 % erreicht.

Bei der Verwendung von Deloxan ASP I/9 als Katalysator, konnten in beiden Ketonisierungsreaktionen Selektivitäten von über 80 % beobachtet werden, während die Umsätze des ungesättigten Alkohols nie höher als bei 60 % lagen.

Um Ketonisierungsreaktionen mit herkömmlichem Lösungsmittel (Toluen), ohne Lösungsmittel und mit “überkritischem” Kohlendioxid (“scCO_2”) als Lösungsmittel, das in anderen Reaktionen die Durchmischung der Reaktanten verbesserte, zu vergleichen, wurden Experimente in einem absatzweise betriebenen Reaktorsystem (Autoklav) durchgeführt. Die Ketonisierung von 2-Methyl-3-butyn-2-ol in “scCO_2” erreichte nicht einmal halb so hohe Ausbeuten, wie diejenige mit Toluen als Lösungsmittel. Die Dehydrolinalool-Ketonisierung andererseits, zeigte mit “überkritischem” CO_2 Ausbeuten des gewünschten Produkts, relativ zu Dehydrolinalool, die ungefähr dreimal so hoch waren, wie jene mit herkömmlichem Lösungsmittel. Andererseits musste aber festgestellt werden, dass die Anwendung von “scCO_2” im Vergleich zum Versuch ohne Lösungsmittel zu keiner Verbesserung der Resultate führte. Somit brachte die Anwendung von “überkritischem” CO_2 als Lösungsmittel keine erkennbaren Vorteile.

Um eine Einsicht in die chemischen Wechselwirkungen zu bekommen, die der Vinylether (MP) auf den aktiven Stellen des ASP I/9 Katalysators (enthält

Sulfonsäuregruppen) respektive der sulfatisierten und TiO_2-modifizierten Kieselsäure (enthält Schwefelsäuregruppen) eingeht, wurde die ATR-IR-Spektroskopie (*in situ* attenuated total reflection infrared spectroscopy) angewendet. Schnelle Hydrolyse wird beobachtet, die jedoch nicht auf die sauren Zentren angewiesen ist. Das resultierende Aceton wird überwiegend auf SiOH Gruppen adsorbiert. Durch die sauren Zentren gefördert, kann eine weitere Umwandlungsreaktion auf dem Katalysator beobachtet werden. Das zeitliche Verhalten der ATR Signale von Aceton und vom Produkt deutet darauf hin, dass die weitere Reaktion wahrscheinlich aus einer Kondensation von 2-Methoxypropen und Aceton besteht. Zu Beginn des Versuchs wird Produkt gebildet und Hydronium-Ionen verschwinden von der Katalysatoroberfläche. Nach der Desorption des Reaktionsproduktes erscheinen die Hydronium-Ionen wieder in hohem Mass auf dem Katalysator, der absorbierte Schwefelsäure enthält, während sie zu einem geringeren Masse wieder auf dem Katalysator erscheinen, der Sulfonsäuregruppen enthält. Die zwei untersuchten sauren Katalysatoren unterscheiden sich ziemlich stark in den relativen Konzentrationen an Brønsted- und Lewis-Säurezentren, was den Unterschied bezüglich der relativen Konzentration des Zwischenprodukts und des Produktes in der beobachteten Folgereaktion erklären kann.

Die kombinierten kinetischen und spektroskopischen Studien zeigten, dass die Anwendung von festen Säuren in der Saucy-Marbet Ketonisierungsreaktion eine Alternative zu den herkömmlichen homogenen Katalysatoren, die bisher in feinchemischen Synthesen benutzt wurden, bieten kann. Obschon die hohen Ausbeuten der homogenen Katalysatoren nicht erreicht werden konnten, haben heterogene Katalysatoren den Vorteil der einfachen Trennung vom Produktstrom und würden folglich zu weniger aufwändigen Produktreinigungs-Prozessen führen. Zudem bietet die heterogene Katalyse Vorteile bezüglich einer möglichen kontinuierlichen Reaktionsführung.

Chapter 1

Introduction

1.1 General Aspects

In fine chemical industrial syntheses, condensation reactions of an unsaturated alcohol (I) and an unsaturated ether (II) to form an unsaturated ketone (III) with higher molecular weight are of special interest as intermediate reactions for the production of long-chain compounds [1-6].

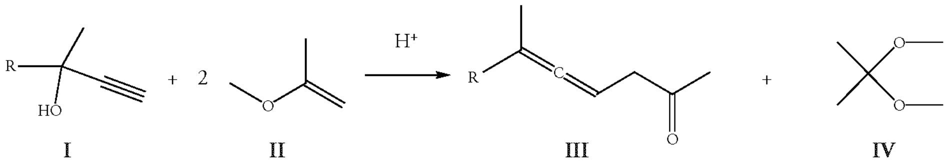

Fig. 1-1: Reaction scheme of Saucy-Marbet ketonization reaction.

These condensation reactions are used in flavour, fragrance, vitamin and other fine chemical syntheses and were first investigated by G. Saucy and R. Marbet. [7-11]

In the present work two different chain prolongation reactions of the stated Saucy-Marbet-type (Figure 1-1), with different chain lengths of the unsaturated alcohol, were studied more thoroughly.

1.2 Claisen-Type Rearrangement Reactions

In 1912 L. Claisen discovered the thermal rearrangement reaction of allyl vinyl ether to 4-pentenal that was later named after him (Figure 1-2) [12-14].

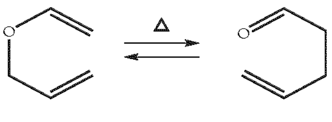

Fig. 1-2: Thermal Claisen rearrangement reaction.

Based on his studies, many different related rearrangement reactions were investigated and are still used in countless industrial processes. Several reviews give an overview over related rearrangement types [7, 15-17]. Further studies on the Claisen rearrangement reaction and its applications can be found in [18-22]. Only few of these rearrangement reactions will be discussed in this chapter; main attention will be directed to those which can be used to produce similar compounds as reaction products of the aforementioned Saucy-Marbet ketonization reaction.

One of the most popular Claisen rearrangement related reactions to produce unsaturated ketones, as for example pseudoionone (compound VIIa in Table 1-1, which is used as an intermediate product in industrial vitamin and flavour production), is the Carroll rearrangement reaction (first discussed in 1940) [23, 24]. As in the already presented ketonization reaction from Saucy

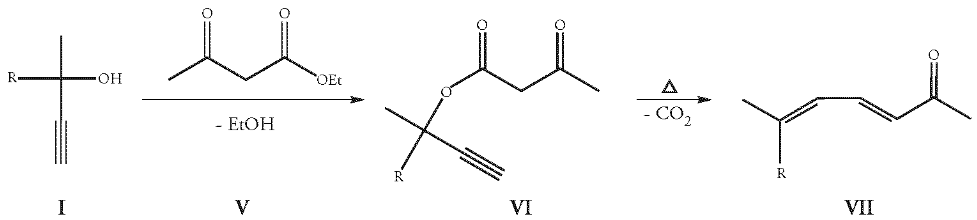

Fig. 1-3: Application of the Carroll rearrangement reaction, industrially used to produce pseudoionone.

and Marbet, Carroll also used an unsaturated alcohol as reactant. But instead of an unsaturated ether, alkyl acetoacetates were chosen to produce unsaturated ketones (Figure 1-3) [7, 25, 26].

Another pathway to produce pseudoionone, is the base catalyzed aldol condensation reaction of citral, which can be produced as described in [27-29], and acetone (Figure 1-4) [25]. Although in this reaction type no rearrangement step takes place, it is stated in this context, because it is an industrially important reaction for production of vitamin intermediates and also because it was already successfully carried out with heterogeneous catalysts [30-32].

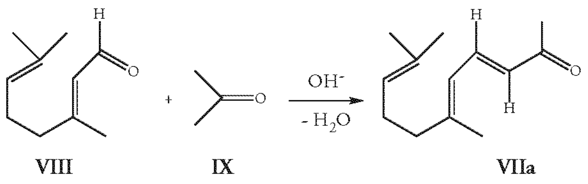

Fig. 1-4: Production of pseudoionone by base catalyzed aldol condensation reaction of citral and acetone.

W. Kimel and N. Sax described in 1957 a total synthesis of pseudoionone, starting from acetone and acetylene [33-35]. In one of the last reaction steps, dehydrolinalool was converted to dehydrolinalyl acetoacetate, by reaction with diketene (4-methylene-2-oxetanone). Finally, pyrolysis at 170-190 °C caused withdrawing of CO_2 and a mixture of ketones was produced, mainly consisting of pseudoionone.

In the past, various other routes to produce unsaturated ketones, which can be used as intermediates in fine chemical syntheses, as for example pseudoionone, were investigated [36-41].

R. Marbet and G. Saucy presented in 1960 a new method to synthesize pseudoionone by a condensation reaction of dehydrolinalool and 2-ethoxypropene [42], which was also the topic of studies by Julia et al. in 1964 [5]. The same reaction, but with 2-methoxypropene instead of 2-ethoxypropene, was then more thoroughly discussed in 1967, again by Saucy and Marbet [2, 3, 6, 43, 44]. Figure 1-5 shows a more detailed reaction scheme for the various reaction steps, whose intermediate products could be isolated and were identified [2, 4, 45-47]. The first condensation step of an unsaturated alcohol I and an unsaturated ether II to intermediate product III' is acid catalyzed. Also the next step, elimination of methanol, which then reacts further with the unsaturated ether II to form a ketal (IV, see Figure 1-1), is acid catalyzed. Finally, thermal, intramolecular rearrangement of III" to III takes place. By-product IV (2,2-dimethoxypropane) can be recycled with a (heterogeneously) acid catalyzed reaction to form 2-methoxypropene that can be reused in the ketonization reaction [44]. The reaction can be carried out in hydrocarbons such as benzene, toluene, hexane, heptane, isooctane and petroleum ether or without solvent [3].

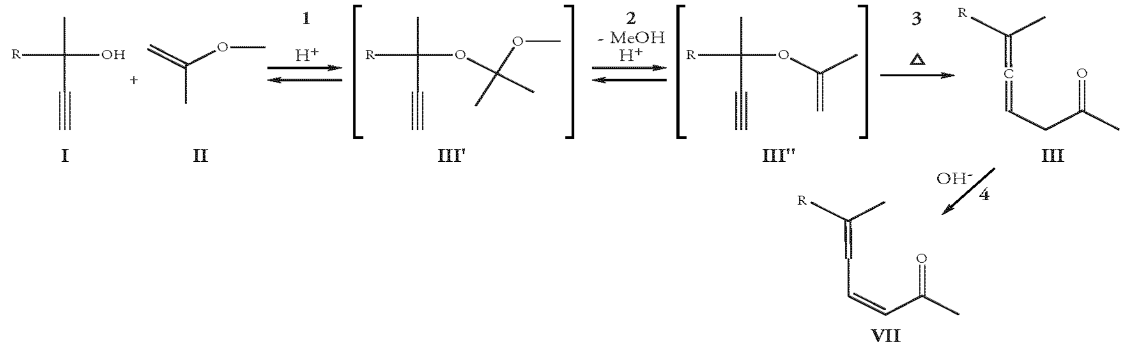

Fig. 1-5: Detailed reaction scheme for the ketonization reaction.

In various publications [48-50], rearrangements of Ia (dehydrolinalool) were described that are undesired if product VIIa (pseudoionone) should be gained, but can also be useful for synthesis of intermediate products used in fragrance and flavour production (Figure 1-6).

The described Saucy-Marbet condensation reaction can also be carried out with alkenes instead of alkynes as reactants [1, 51, 52].

Table 1-1 shows a list of the compound numbers and their corresponding names used in the reaction schemes (Figures1-1 to 1-6).

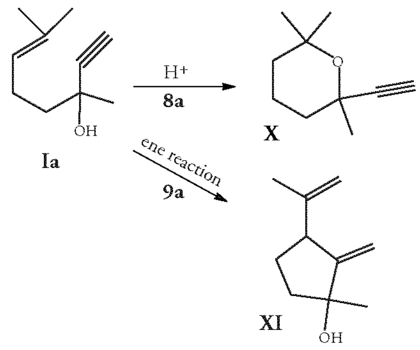

Fig. 1-6: Possible side reactions by rearrangements of DLL.

1.3 Use of Solid Acid Catalysts

The first reaction step of the Saucy-Marbet ketonization reaction is acid catalyzed. Originally, the following homogeneous catalysts were used to catalyze this reaction step: strong mineral acids, e.g. sulfuric acid, phosphoric acid; acid-reacting salts, e.g. potassium bisulfate; organic acids, e.g. p-toluenesulfonic acid, oxalic acid, trichloracetic acid; "Lewis acids", e.g. zinc chloride or boron trifluoride ethyl etherate [2, 3, 43]. These homogeneous catalysts were useful to reach high yields of the desired ketone, but on the other hand, catalyst removal from the product mixture by distillation or extraction was, especially for industrial applications, energetically expensive. Even more, various homogeneous acids were often difficult to handle, dangerous and toxic for the environment. All these reasons lead to the idea of exchanging homogeneous catalysts with heterogeneous acids that have advantages in these areas. Batch reactor studies showed that the application of a heterogeneous catalyst is feasible [53].

In various reviews potential solid acids and possible applications of these materials are discussed in detail [54-63]. Other publications consider measurements of catalyst properties, as for example catalyst acidity [64-69].

Possible solid acids to catalyze the ketonization reaction are the following (incomplete list):

- Ion exchange catalysts [10, 70-78]

Table 1-1: Compounds used in reaction schemes (Figures 1-1 to 1-6).

Compound	R	Name(s)
Ia	4-methyl-3-pentene	DLL; dehydrolinalool; 3,7-dimethyl-oct-6-en-1-yn-3-ol
Ib	methyl	MB; 2-methyl-3-butyn-2-ol
II		MP; 2-methoxypropene
IIIa	4-methyl-3-pentene	C13AK; 6,10-dimethyl-4,5,9-undecatrien-2-one
IIIb	methyl	C8AK; 6-methyl-4,5-heptadien-2-one
III'a	4-methyl-3-pentene	DLLAdd; 3-(1-methoxy-1-methylethoxy)-3,7-dimethyl-6-octen-1-yne
III'b	methyl	MBAdd; 3-(1-methoxy-1-methylethoxy)-3-methyl-1-butyne
III"a	4-methyl-3-pentene	3,7-dimethyl-3-[(1-methylethenyl)oxy]-6-octen-1-yne
III"b	methyl	3-methyl-3-[(1-methylethenyl)oxy]-1-butyne
IV		DMP; 2,2-dimethoxypropane
V		ethyl acetoacetate; 3-oxo-butanoic acid ethyl ester
VIa	4-methyl-3-pentene	3-oxo-butanoic acid-1-ethynyl-1,5-dimethyl-4-hexenyl ester
VIb	methyl	3-oxo-butanoic acid 1,1-dimethyl-2-propynyl ester
VIIa	4-methyl-3-pentene	PI; pseudoionone; 6,10-dimethyl-3,5,9-undecatrien-2-one
VIIb	methyl	MH; 6-methyl-3,5-heptadien-2-one
VIII		citral; 3,7-dimethyl-2,6-octadienal
IX		acetone; 2-propanone
X	4-methyl-3-pentene	ETTP; 2-ethynyltetrahydro-2,6,6-trimethyl-2H-pyran
XI	4-methyl-3-pentene	1-methyl-2-methylene-3-(1-methylethenyl)-cyclopentanol

- Sulfonated polysiloxanes (e.g. Deloxan ASP) [54, 55, 79, 80]
- Zeolites [54, 55, 60, 61, 81-84]
- Nafion-silica composites [55, 61, 85-91]

- Clays [84, 92, 93]
- Sulfated metal oxides [54, 55, 61, 94]
- Heteropoly acids [54, 55, 61, 84, 95-97]

In the preceding list of catalysts, some acids, as for example Nafion-resins, sulfated metal oxides and heteropoly acids, can even behave as solid superacids [91, 96, 98-102].

The following list presents a few reactions that were already successfully carried out with solid acids, many other applications also exist:

- Alkylations [57, 61] with ion exchange catalysts [61, 72, 73, 103, 104], with sulfonated polysiloxanes [79, 80, 104, 105], with zeolites [55, 61, 106-110], with Nafion [54, 55, 61, 85-90, 102, 111], with clays [84], with sulfated metal oxides [55, 61, 102, 109, 112] and with heteropoly acids [54, 55, 61, 84, 95, 97, 113].
- Condensations with ion exchange catalysts [71-73, 114-118], with sulfonated polysiloxanes [54, 55, 79, 80], with zeolites [55, 119-121], with Nafion [86, 90, 114, 115], with clays [84] and with heteropoly acids [55, 113].
- Isomerizations with ion exchange catalysts [71, 122, 123], with zeolites [55, 107, 122], with Nafion [85, 87, 88, 102, 122, 123], with sulfated metal oxides [55, 102] and with heteropoly acids [84, 97].
- Esterifications with ion exchange catalysts [70, 73, 124], with sulfonated polysiloxanes [79, 80], with zeolites [55], with Nafion [86, 90], with sulfated metal oxides [55, 102] and with heteropoly acids [55, 84, 113].
- Dehydrations (of alcohols) with ion exchange catalysts [70, 73, 124], with sulfonated polysiloxanes [125], with zeolites [55, 59], with Nafion [55, 126], with sulfated metal oxides [55] and with heteropoly acids [55, 84, 113].
- MTBE-synthesis with ion exchange catalysts [70, 73, 127, 128], with sulfonated polysiloxanes [79] and with zeolites [55].

1.4 Use of "Supercritical" Fluids

In the last few years, application of "supercritical" fluids ("SCFs") as media for heterogeneously catalyzed reactions became more and more popular [129-131]. Due to their unique properties, "SCFs" became renowned alternatives for conventional solvents. For convenience and to prevent misunderstandings, in this work the term "supercritical" (in quotes) is used for a dense fluid phase at temperatures above its mixture critical point, regardless of further liquid phases present [132]. Satisfactory solubilities, ability for dissolution of coke residues from heterogeneous catalysts, low viscosities and facile tunability are only a few advantages, compared to conventional solvents, to point out. Supreme physical properties between those of a liquid and a gas make "SCFs" interesting for chemical reactions, especially concerning mass transfer limiting aspects of reactants.

A few examples of recent studies on heterogeneously catalyzed reactions with "supercritical" fluids as solvents should emphasize these arguments: alkylations with sulfonated polysiloxanes [104, 105], dehydrations of alcohols with sulfonated polysiloxanes and ion exchange catalysts [125], condensations with ion exchange catalysts [118] and alkylations with zeolites [61, 109, 110]. Recently, supercritical solvents have also successfully been used in the heterogeneously catalyzed synthesis of D,L-α-tocopherol [133, 134].

In the present work, the applicability of "supercritical" CO_2 as solvent for the Saucy-Marbet ketonization reaction was investigated.

1.5 Scope of the Thesis

The main purpose of this thesis was to find a suitable heterogeneous catalytic route for the ketonization of dehydrolinalool. This would provide the opportunity to perform the reaction in a continuous reactor system. Another aspect was the parametric sensitivity and the applicability of "supercritical" solvents. To test the general applicability of the heterogeneous process, another ketonization including a low molecular unsaturated alcohol (2-methyl-3-butyn-2-ol) was also investigated. In a final step attenuated total reflection infrared spectroscopy (ATR-IR) was applied to gain some insight of the molecular processes occurring at the acid-solid interface of the catalysts.

1.6 Abbreviations and Symbols used in this Thesis

Abbreviations and symbols used in this thesis are collected in Table 1-2.

Table 1-2: List of abbreviations and symbols used in this thesis.

A	reactant (DLL, MB resp. MP)
ATR	Attenuated Total Reflection
C13AK	C13-allene ketone (6,10-dimethyl-4,5,9-undecatrien-2-one)
C8AK	C8-allene ketone (6-methyl-4,5-heptadien-2-one)
DAA	diacetone alcohol (acetone dimer, 4-hydroxy-4-methyl-2-pentanone)
DLL	dehydrolinalool (3,7-dimethyl-oct-6-en-1-yn-3-ol)
DLLAdd	DLL-MP-addition product (3-(1-methoxy-1-methylethoxy)-3,7-dimethyl-6-octen-1-yne)
DMP	2,2-dimethoxypropane
d_p	particle diameter
F_i	molar flow rate of species i (moles s^{-1})
F_{i0}	entering molar flow rate of species i (moles s^{-1})
ETTP	DLL-rearrangement product (2-ethynyltetrahydro-2,6,6-trimethyl-2H-pyran)
GC	gas chromatography
IP	isophorone (3,5,5-trimethylcyclohex-2-enone)
L	catalyst bed length
LHSV	Liquid Hourly Space Velocity
MB	2-methyl-3-butyn-2-ol
MBAdd	MB-MP-addition product (3-(1-methoxy-1-methylethoxy)-3-methyl-1-butyne)
MeOH	methanol
MH	6-methyl-3,5-heptadien-2-one
MP	2-methoxypropene
MPD	2-methoxypropene dimer (2,4-dimethoxy-4-methyl-1-pentene)
MSO	mesityloxide (4-methyl-3-penten-2-one)
n	reaction order
N_i	number of moles of species i after reaction (moles)

Table 1-2: List of abbreviations and symbols used in this thesis.

N_{i0}	number of moles of species *i* before reaction (moles)
p	pressure
P	product (C13AK, and C8AK, respectively)
PI	pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one)
PSA	1-propane sulfonic acid
PTFE	polytetrafluoroethylene
S	selectivity
“sc”	“supercritical”
“SCFs”	“supercritical” fluids
T	temperature
X	conversion
Y	yield

Chapter 2

Experimental

The experimental setup for this work consisted mainly of a continuous flow reactor, used for the catalytic studies. Investigations of applicability of "supercritical" CO_2 as solvent for the ketonization reaction were carried out in a batch reactor system. To gain more profound knowledge about the reaction course an ATR-IR-system was used. These three systems, the analytical setup, as well as the employed catalysts and their characterization will be described in this chapter, which also includes a troubleshooting part, where several issues, that had to be faced during the course of this work, will be discussed.

2.1 Experiments in Continuous Flow Reactor System

2-methoxypropene (MP, Teranol AG), 2-methyl-3-butyn-2-ol (MB, Fluka, > 99 %), dehydrolinalool (DLL, Teranol AG), 2,2-dimethoxypropane (DMP, Teranol AG), pentadecane (Fluka, > 98 %), n-hexane (Merck, for spectroscopy) and 1-butanol (Acros Organics, > 99.5 %) were used as received.

In Figure 2-1 the apparatus used for catalytic tests with continuous flow reaction conditions is shown schematically. The reactions were carried out in a 38 ml stainless-steel fixed-bed tubular reactor (12 mm inner diameter; downward stream concept) which was designed for pressures and temperatures up to 200 bar and 300 °C. The reactor was heated electrically by two heating-jackets, one for the reactor head (static mixer) and another for the fixed-bed part of the reactor. The reaction temperature was monitored by an axially adjustable thermocouple inside the catalyst bed (see also Figure 2-2). The reactants were fed into the reactor by two HPLC-pumps (Jasco PU-980). Pressure was controlled by a back pressure regulator (Tescom, Series 26-1724), located right after the

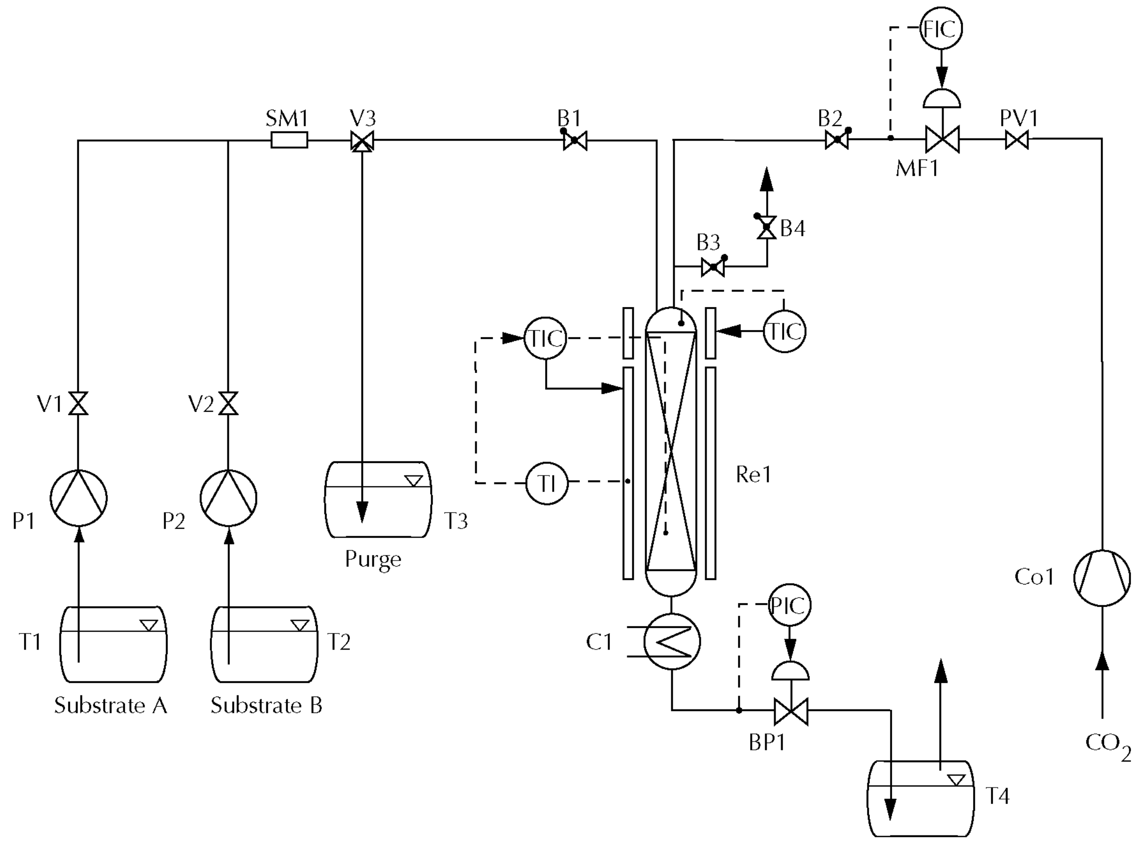

Fig. 2-1: Schematic illustration of the continuous flow reactor system used for catalytic experiments. T: tank, V: valve, Co: compressor, P: HPLC-pump, SM: static mixer, B: bursting valve, Re: reactor, TI: temperature indicator, TIC: temperature controller with indicator, C: cooling system, BP: back pressure regulator, PIC: pressure controller with indicator, MF: massflow controller, FIC: flow controller with indicator.

reactor outlet. Additionally, by using a CO_2-compressor (PM-101, NWA) and a combination of a flow meter (HI-Tec Bronkhorst, El-Flow) and a needle valve (Kämmer), carbon dioxide could be fed to the reactor.

If not otherwise stated, standard conditions were used for the experiments: 110 °C, 50 bar, molar ratio MP/DLL resp. MP/MB=3, total flow rate: 0.6 ml min^{-1} (for experiments with DLL) resp. 0.54 ml min^{-1} (for experiments with MB), 4 g of conditioned catalyst (see Chapter 2.2.2).

After reaching the desired pressure of 50 bar by pumping both reactants simultaneously to the system (1.2 ml MP min^{-1} and 0.6 ml DLL min^{-1} resp.

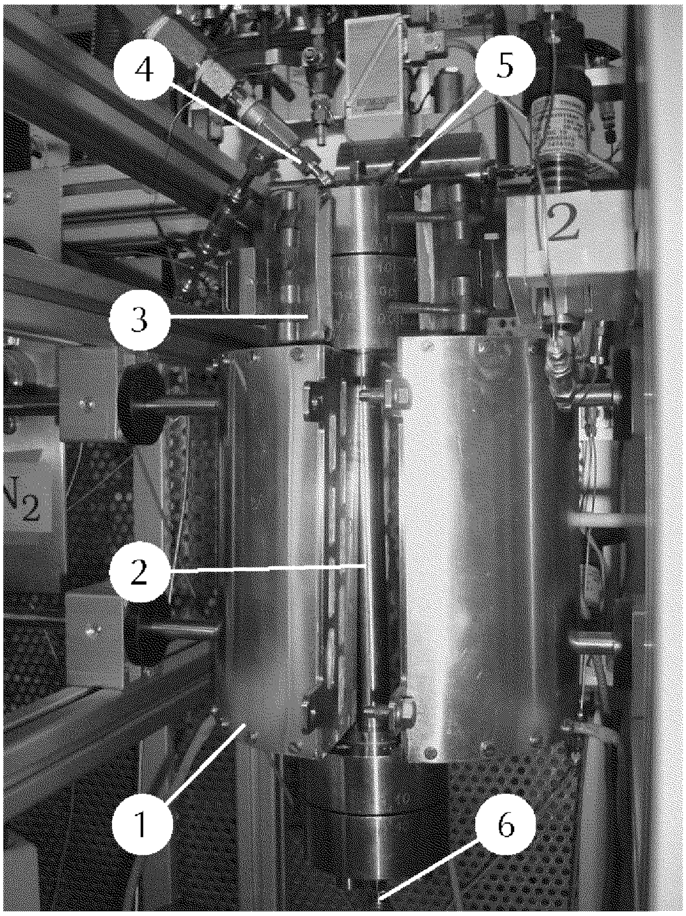

Fig. 2-2: Continuous flow reactor system, detail view. 1: reactor heating jacket, 2: reactor, 3: reactor preheating zone, 4: gas stream reactor inlet, 5: liquid stream reactor inlet, 6: reactor outlet.

0.42 ml MB min^{-1}) heating was started. Then reactant flows were kept at constant rates for 30 min to flush undesired products from the system. Finally, flows were reduced to "standard flows". Samples of 1 ml (two samples at reactor inlet and two samples at T4 inlet to calculate conversion, selectivity and yield) were taken after 4 h of stable conditions.

Reactor flow conditions can be predicted, if the following relation is calculated [135]: $(L/d_p) > (20n/Pe_a)\ln(C_0/C)$.

As a rule of thumb, plug flow conditions can be assumed if $(L/d_p) > 100$ (for first order reaction).

In the case of 4 g of Deloxan ASP I/9 as catalyst (L: 95 mm, d_p: 0.1-0.4 mm), the ratio of (bed length (L) / particle diameter (d_p)) is at least 238. Thus, plug flow conditions in the reactor can be assumed for experiments in the continuous flow system.

Conversion, selectivity and yield of desired product related to DLL, MB resp. MP in the continuous flow reactor were calculated as follows [136]:

- Conversion: $X = (F_{A0} - F_A) / F_{A0}$
- Selectivity: $S = F_P / (F_{A0} - F_A)$
- Yield: $Y = X * S$

with F_i: molar flow rate of species i (moles s^{-1}); F_{i0}: entering molar flow rate of species i (moles s^{-1}); A: reactant (DLL, MB resp. MP); P: product (C13AK, and C8AK, respectively).

2.2 Troubleshooting

2.2.1 Sampling

Initially samples were taken with a plunger-operated pipetter (Brand Transferpette®) with exchangeable 1 ml syringe tips. Due to different viscosities of the samples, this syringe type, which bases on a constant pulling force and not on volumetric measuring, was not precise enough (visible volume differences between different samples, especially between samples before and after reaction). Only catalyst screening experiments for DLL-ketonization reaction (Chapter 3.2) were measured with these syringes. For all the following experiments single use 1 ml syringes (Codan Medical ApS, Primo), which did not show the discussed problems with viscosity differences, were used. Experiments, in which both sampling devices were used, showed that qualitative conclusions taken from the catalyst screening are still valid.

2.2.2 Irreproducible Results with Untreated Catalyst

Due to high activity of untreated Deloxan ASP I/9 catalyst for the observed ketonization reactions, measurements after short periods of constant reaction conditions were not satisfactory reproducible. Conditioning of the catalyst for

40 h for DLL-ketonization resp. 24 h for MB-ketonization at “standard conditions” was necessary in order to get pseudo-stationary state conditions (see also Chapter 3.4 and Chapter 4.3).

2.2.3 Product Loss

Product loss due to low boiling points of used reactants (MP and MB) led to stoichiometrically impossible conversion- and selectivity-results (negative conversions and selectivities higher than 100 %). By using CO_2 as solvent, a part of the product stream was removed from the system together with the solvent stream.

The seal used in the back pressure regulator was continuously harmed by aggressive substances (MP, CO_2, polymeric substances etc.) and had to be exchanged every few weeks to prevent loss of low boiling substances from the system.

These problems with product loss showed the impossibility to use this continuous system for experiments with “$scCO_2$” as solvent and made experiments in a batch reactor system unavoidable.

2.3 Experiments in Batch Reactor System

2-methoxypropene (MP, Teranol AG), 2-methyl-3-butyn-2-ol (MB, Fluka, > 99 %), dehydrolinalool (DLL, Teranol AG), toluene (J. T. Baker, > 99.5 %), CO_2 (PanGas, liquid carbon dioxide from bottle with plunge pipe, 99.995 %), pentadecane (Fluka, > 98 %), n-hexane (Merck, for spectroscopy) and 1-butanol (Acros Organics, > 99.5 %) were used as received.

Figure 2-3 shows a schematic illustration of the batch reactor system used for catalytic experiments (see also Figure 2-4). The 100 ml stainless steel autoclave (Parr 4560 Mini Reactor) was equipped with a mechanical stirrer and was heated electrically by a heating jacket. The reaction temperature was monitored by an adjustable iron-constantan-thermocouple inside the reactor.

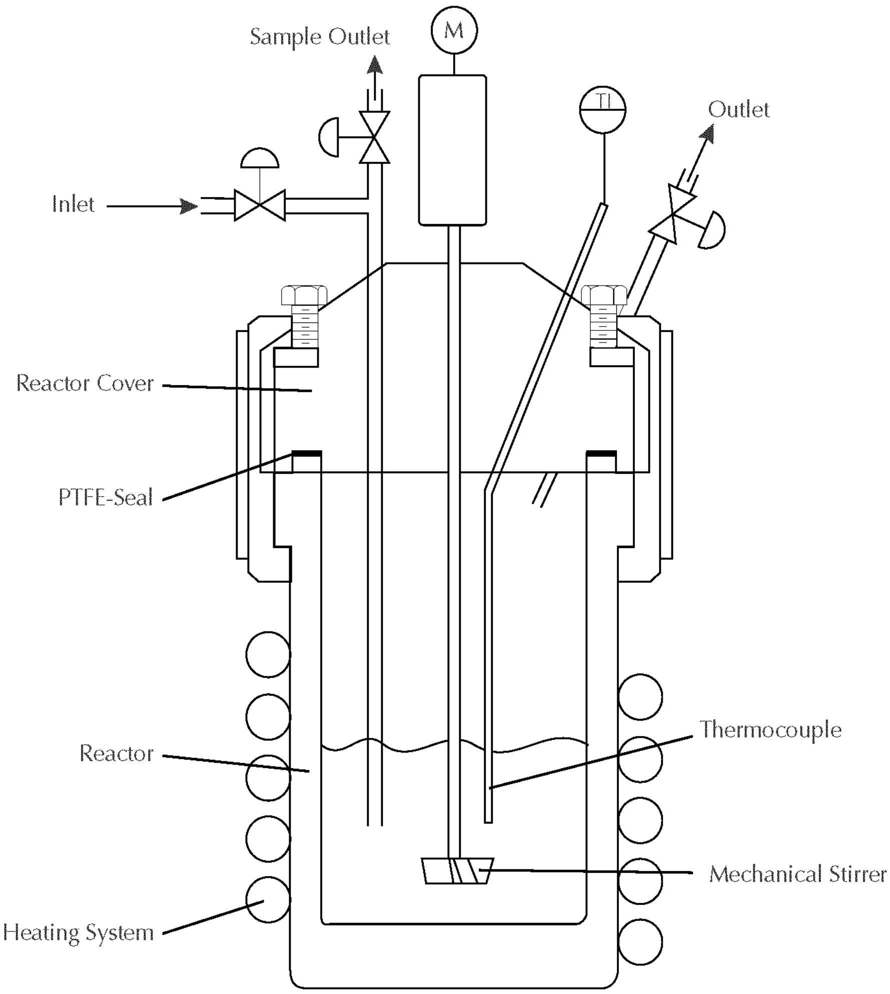

Fig. 2-3: Schematic illustration of the autoclave system used for catalytic experiments.

After filling the reactants (20 ml, with a molar ratio MP/DLL resp. MP/MB of 3), the solvent (75 ml in the case of toluene as solvent) and the catalyst (0.5 g Deloxan ASP I/9; conditioned for 40 h (DLL) resp. 24 h (MB) in the continuous flow system at standard conditions) into the reactor, the autoclave was closed and placed into the heating system. The mechanical stirring was set to 500 rpm and electrical heating was started (setpoint 110 °C). Depending on experimental conditions, CO_2 resp. N_2 were fed to the reactor to reach the desired pressure resp. to add the solvent (in the case of CO_2 as solvent). After 240 min (heating time included) reactor heating was turned off and after another 150 min of cooling to RT, inside pressure was released to atmospheric

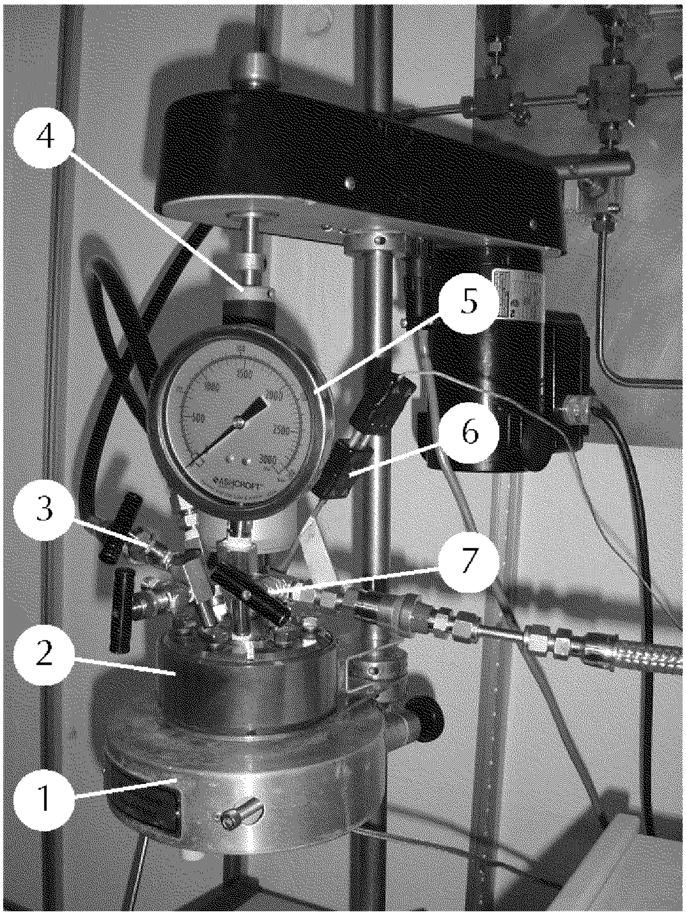

Fig. 2-4: Autoclave reactor system, detail view. 1: heating jacket, 2: reactor, 3: inlet valve, 4: mechanical stirrer, 5: manometer, 6: thermocouple, 7: outlet valve.

pressure by carefully opening the reactor outlet valve. To determine conversion, selectivity and yield, samples of 1 ml each were taken before and after reaction.

The following definitions [136] were used to calculate conversion, selectivity and yield of desired product related to DLL, MB resp. MP in the batch reactor:

- Conversion: $X = (N_{A0} - N_A) / N_{A0}$
- Selectivity: $S = N_P / (N_{A0} - N_A)$
- Yield: $Y = X * S$

with N_i: number of moles of species i after reaction (moles); N_{i0}: number of moles of species i before reaction (moles); A: reactant (DLL, MB resp. MP); P: product (C13AK resp. C8AK).

2.4 Analytical Setup

Composition of reactor inlet and outlet streams (continuous reactor) as well as of reaction mixtures (batch) were determined using a ThermoFinnigan (TraceGC) gas chromatograph (carrier gas: helium) with a fused silica capillary column (30 m * 0.25 mm Optima-5-0.25 m). 0.14 g pentadecane was added (as a standard) to 1 ml of sample and 20 ml hexane (for experiments with DLL) resp. 20 ml 1-butanol (for experiments with MB) was used as solvent for the samples for GC-analysis. 1 µl of this solution was injected in a split/splitless injector at 250 °C. The oven temperature was first held at 34 °C. After 9 min it was heated to 240 °C with a rate of 9 °C min^{-1} and then held at this temperature for 6 min. Products were detected with a flame ionisation detector (FID) at 280 °C. For quantitative analysis, calibration curves were recorded to calculate conversion, selectivity and yield from the measured peak areas (related to the internal standard peak area).

2.5 Catalysts and Characterization

Various types of solid acids were tested as potential catalysts for dehydrolinalool-ketonization. A complete list of used catalysts is presented in Table 2-1 (alphabetically sorted by supplier). All catalysts used for catalyst screening experiments were applied as received.

A selection of catalysts, which attained the highest yields of desired product C13AK, were characterized by nitrogen-physisorption. A comparison of measured BET surface areas and average pore diameters with corresponding values from supplier's data sheets is presented in Table 2-2. Additionally, pore size distributions for Deloxan ASP I/9- and sulfated and TiO_2-modified amorphous SiO_2-samples are shown in Figure 2-5 and Figure 2-6, respectively. The corresponding catalytic results of the selected catalysts can be found in Table 3-1 and are discussed in Chapter 3.2.

Table 2-1: List of tested catalysts for DLL-ketonization reaction.

Supplier	Type	Description[a]
Bayer	K 2411	Polymer, strongly acidic, macroporous, contains sulfonic acid groups, H-form
	K 2441	Polymer, strongly acidic, macroporous, contains sulfonic acid groups, H-form
	K 2621	Polymer, strongly acidic, macroporous, contains sulfonic acid groups, H-form
	K 2641	Polymer, strongly acidic, macroporous, contains sulfonic acid groups, H-form
	Lewatit SP 112 WS	Cation exchange catalyst made of polystyrol, strongly acidic, macroporous, contains sulfonic acid groups as functional groups, Na-form
	Lewatit S 2328	Cation exchange catalyst made of polystyrol, strongly acidic, macroporous, contains sulfonic acid groups as functional groups, H-form
CU Chemie Uetikon AG	Zeocat PB/H	Beta-zeolite, H-form
	Zeocat FM-8/25H	Mordenite, H-form
	Zeocat PZ-2/100H	ZSM-5 zeolite, H-form
	NaHY	Zeolite Y, Na < 1 %, H-form
Degussa	Deloxan ASP I/9	Alkyl sulfonic acid polysiloxane
	Deloxan ASP IV/6*2	hydrophobic macroporous organofunctional polysiloxane, H-form
	Wessalith DAY-F20	Organophilic and hydrophobic zeolite Y
	Sulfated amorphous SiO_2	Sulfated amorphous SiO_2
	Sulfated and TiO_2-modified amorphous SiO_2	Titanium dioxide modified, sulfated amorphous SiO_2, FBC 9/165

Table 2-1: List of tested catalysts for DLL-ketonization reaction.

Supplier	Type	Description[a]
Engelhard	Nafion/SiO_2	Strongly acidic sulfonic acid, on silica support
Fluka	Nafion NR50	Strongly acidic sulfonic acid, H-form
	Nafion 117 Solution	Nafion, ~5% in a mixture of lower aliphatic alcohols and water
	Magnesium Oxide	98.0% (KT, based on calcined substance)
Mitsubishi	Diaion RCP145HD	Cation exchange resin, H-form
Purolite	CT151	Cation exchange resin, macroporous, H-form
	CT165	Cation exchange resin, macroporous, H-form
	CT169	Cation exchange resin, macroporous, H-form
	C175	Cation exchange resin, macroporous, H-form
Resin Tech Inc.	CG-8-H RTP-6286	Cation exchange resin, gel, 8 % crosslinked, H-form
	CG-10-H RTP-5787	Cation exchange resin, gel, 10 % crosslinked, H-form
	SACMP-H RTI-6808	Anion exchange resin, macroporous, H-form
	SACMP RTI-6807	Cation exchange resin, macroporous, Na-form
	SACMP RTI-6807	Cation exchange resin, macroporous, Na-form
Rohm and Haas	Amberlyst 15Dry	Cation exchange resin made of sulfonized divinylbenzol and styrol-copolymer, strongly acidic, H-form
	Amberlyst 36Dry	Cation exchange resin made of sulfonized divinylbenzol and styrol-copolymer, strongly acidic, H-form
	CSP2	Cation exchange resin, for use in MTBE-reactors, H-form
	CSP3	Cation exchange resin, for use in MTBE/TAME-reactors, H-form

Table 2-1: List of tested catalysts for DLL-ketonization reaction.

Supplier	Type	Description[a]
Veronika Quaschning[b]	SZMEL1	Sulfated zirconium oxide, (MEL: Magnesium Elektron Ltd.)
	SZMEL2	Sulfated zirconium oxide, (MEL: Magnesium Elektron Ltd.)
	Zr251	Sulfated zirconium oxide
Wako	Sulfated Zirconia	Solid superstrong acid catalyst prepared by metal oxide. Zr: 60-70 wt. %

[a] Qualitative descriptions taken from data sheets provided by manufacturers (if not indicated differently).

[b] Catalyst preparation described in [137].

Nitrogen physisorption measurements to determine specific surface areas and average pore diameters of selected catalysts tested in screening experiments were performed at 77 K using a Micromeritics ASAP 2000 instrument. Prior to measurements, samples of about 0.5 g were degassed to 0.1 Pa at 403 K. BET-surface areas and average pore diameters were calculated in a relative pressure range 0.05-0.2 under the assumption that adsorbed nitrogen molecules possess a cross-sectional area of 0.162 nm^2. The Barrett-Joyner-Halenda (BJH) method was applied to the desorption branch of the isotherms to calculate the pore size distributions [64, 141].

For parametric sensitivity studies, Deloxan ASP I/9 (Degussa; Copoly-condensate of propyl(3-sulfonic acid)siloxane and SiO_2; Alkyl sulfonic acid polysiloxane; particle-size: 0.1-0.4 mm; stable for temperatures < 230 °C) was first washed with ethanol, which was then removed by filtering. These steps were repeated three times before the wet catalyst was dried for about 16 h in the oven at 130 °C under vacuum (200 mbar). Fractions of 9.4 g of dried catalyst were used for longterm conditioning steps as described earlier (Chapter 2.2.2).

Further catalyst characterizations with ATR-IR-measurements, including pyridine adsorption, are shown in Chapter 6. The following materials were

Tabelle 2-2: Textural properties of selected catalysts. Values from literature were found in product data sheets provided by suppliers (if not indicated differently).

Catalyst	measured BET surface area [$m^2 g^{-1}$]	measured average pore diameter [nm]	BET surface area [$m^2 g^{-1}$] found in literature	average pore diameter(s)[a] found in literature
Deloxan ASP I/9	588	7	400-600	6-12 nm: 1.0-1.5 ml g^{-1}, >30 nm: 0.3-0.8 ml g^{-1}, total pore volume: 1.5-2.0 ml g^{-1}
sulfated and TiO_2-modified amorphous SiO_2, FBC 9/165	153	23	170	17 nm
Zeocat PB/H	482	7	650	0.64 nm*0.76 nm, 0.55 nm*0.55 nm
NaHY	496	2	720[b] / 903[c] / 697[d] / 657[d]	0.74 nm [b]
Lewatit S 2328	- [e]	- [e]	n. a.[f]	n. a. [f]
Amberlyst 15 Dry	43	27	45	25 nm
Zeocat PZ-2/100H	339	4	400	0.53 nm*0.56 nm, 0.51 nm*0.55 nm
Lewatit SP 112 WS	20	35	350	n. a. [f]
Zeocat FM-8/25H	350	3	> 500	0.65 nm*0.7 nm, 0.26 nm*0.57 nm
Bayer K 2441	12	18	25	40 nm

[a] For zeolites: two main pore sizes.
[b] Values found in [138].
[c] Values found in [139].
[d] Values found in [140].
[e] No measuring of BET surface possible due to problems with degassing of originally wet material. Dramatic colour change during drying step (coinciding structural change and destruction of catalyst possible).
[f] Data not available.

used as received for ATR-IR-measurements: Deloxan ASP I/9 (Degussa), SiO_2 gel 60 (Fluka, puriss. For column chromatography) and sulfated and TiO_2-modified amorphous SiO_2 (Degussa; Consists of < 15 % sulfuric acid, 80-95 % SiO_2 and < 10 % TiO_2; pH < 1.5).

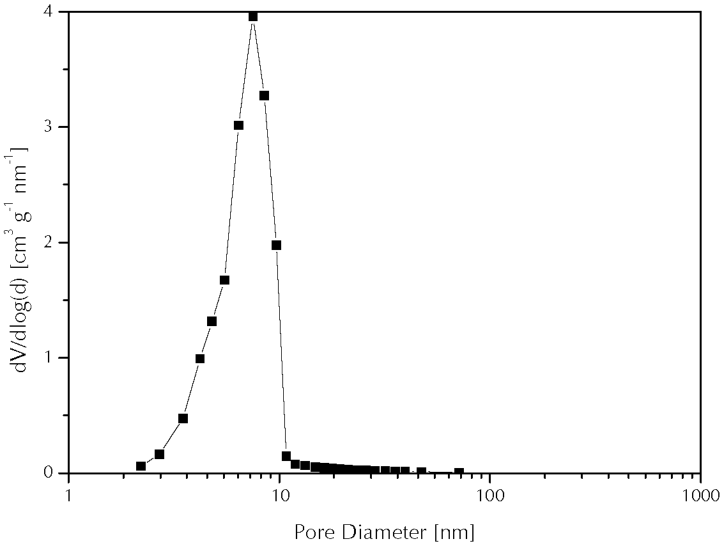

Fig. 2-5: Pore size distribution of Deloxan ASP I/9.

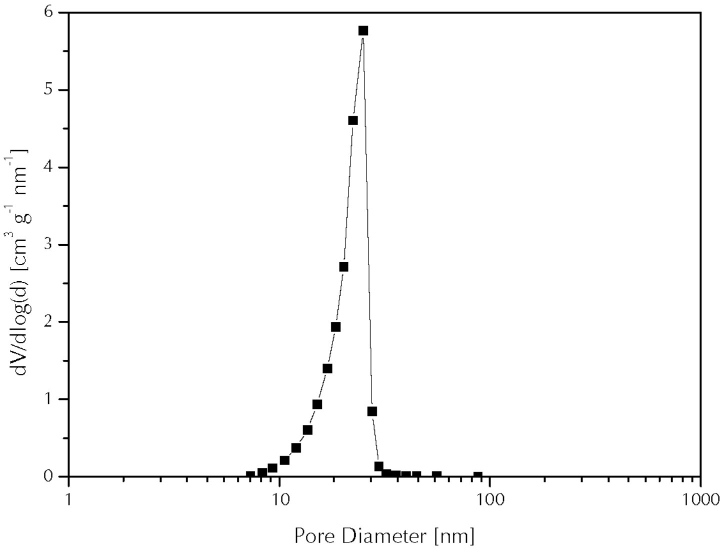

Fig. 2-6: Pore size distribution of sulfated and TiO_2-modified amorphous SiO_2, FBC 9/ 165.

2.6 *In situ* ATR-IR-Spectroscopy

2-methoxypropene (MP, Teranol AG), 2-methyl-3-butyn-2-ol (MB, Fluka, > 99 %), 2,2-dimethoxypropane (DMP, Teranol AG), mesityloxide (MSO, Fluka, > 90 %), acetone (Merck, > 99.8 %), diacetone alcohol (DAA, Fluka, ~ 99 %), pyridine (Fluka, > 99.8 %), 1-propane sulfonic acid (PSA, Fluka, > 99 %), and n-hexane (Merck, for spectroscopy) were used as received.

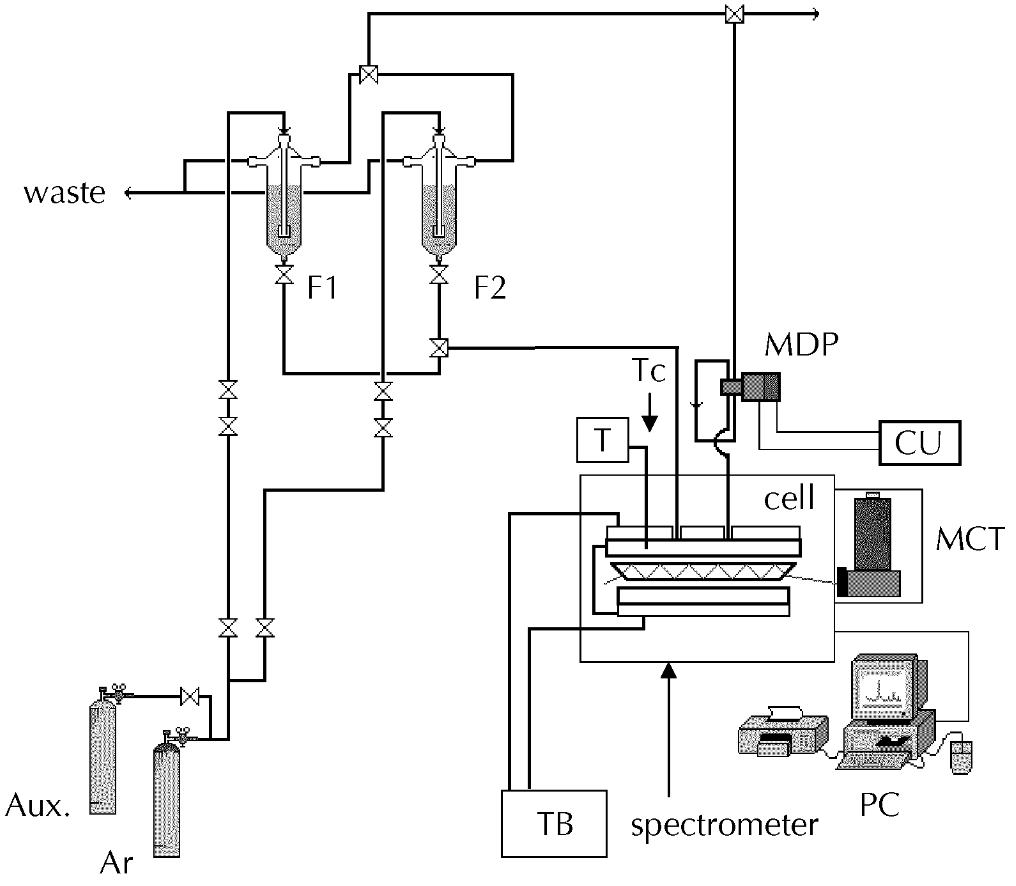

Fig. 2-7: Scheme of the apparatus used for ATR-IR experiments (with kind permission from Dr. D. Ferri). MDP: microdosing pump, CU: control unit (of MDP), MCT: HgCdTe detector, PC: interface to personal computer, Aux.: connection to auxiliary gas, F1 and F2: 150 ml flasks for solutions, T: temperature reader, Tc: thermocouple, TB: thermostat.

SiO_2 gel (Fluka), sulfated and TiO_2-modified amorphous SiO_2 and Deloxan ASP I/9 (Degussa) thin films were prepared from a suspension of the corresponding material (500 mg) in water (for chromatography, Merck, 10 ml). The suspension was deposited on a Ge internal reflection element (IRE) and the solvent evaporated in air. After deposition the films were rinsed with n-hexane to remove loose deposits and the coated IRE was mounted within the walls of a home-made stainless steel infrared cell described elsewhere [142, 143].

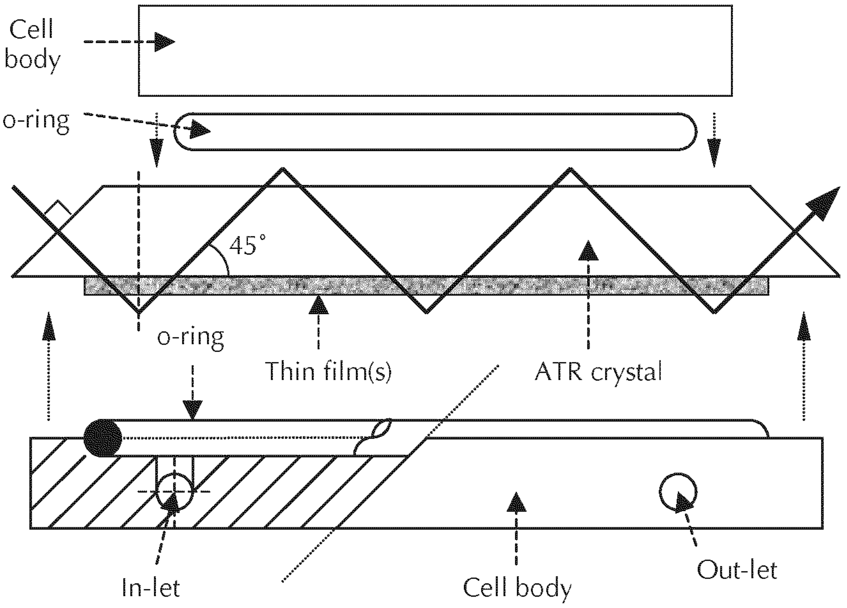

Fig. 2-8: Schematic drawing of the ATR cell (with kind permission from Dr. D. Ferri).

In situ ATR-IR measurements (c.f. Figure 2-7 and Figure 2-8) were performed by flowing a n-hexane solution of the reactant at the desired concentration saturated with argon over the thin film after stabilisation of the IR signal (> 1 h) by flowing Ar-saturated solvent. The adsorption step was followed by a desorption step consisting in the flow of neat solvent saturated with argon. Solutions were pumped through the cell by means of a peristaltic pump at ca. 0.6 ml min^{-1} speed. All measurements were carried out at 25 °C on a Bruker IFS 66 spectrometer equipped with a liquid nitrogen cooled HgCdTe detector by accumulating 200 scans at 4 cm^{-1} resolution. Spectra are reported as absorbance A= -log(I/I$_0$), where I and I$_0$ is the intensity of sample and reference, respectively.

Diffuse reflection infrared spectra (DRIFT) were measured using a Prying Mantis DRIFT accessory together with an environmental chamber

(HVC-DRP-2) from Harrick. Measurements were performed at ambient conditions.

Chapter 3

Dehydrolinalool-Ketonization in Continuous Flow Reactor System

3.1 Introduction

The ketonization of dehydrolinalool (DLL) to form 6,10-dimethyl-4,5,9-undecatrien-2-one (C13AK) is an important reaction step in the synthesis of vitamin E and K. Figure 3-1 shows a scheme of this chain-elongation reaction, which was investigated in this work.

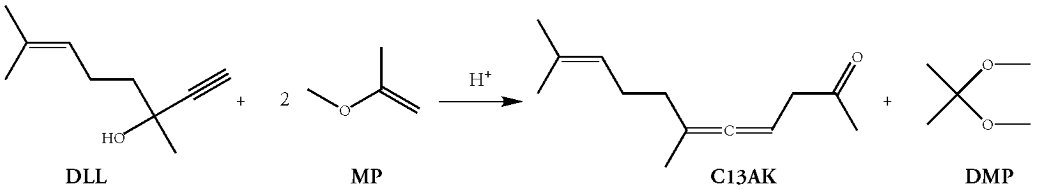

Fig. 3-1: Reaction scheme of dehydrolinalool-ketonization.

In the past, homogeneous catalysts were used to catalyze this Saucy-Marbet ketonization reaction. Although yields of the desired product are satisfactory, catalyst separation and work up of the product mixture raise environmental problems. Besides, the catalyst is not reusable. By using an insoluble solid acid as catalyst, these problems would become obsolete. In homogeneously catalyzed batch reactor experiments (reaction times of up to 24 h) published in literature [2, 6], yields of desired ketones (C13AK or PI) related to DLL of up to 95 % were achieved.

In literature, the DLL-ketonization pathway is described as presented in Figure 3-2 [2, 4, 45-50, 144, 145]. In a first reaction step (1a), dehydrolinalool

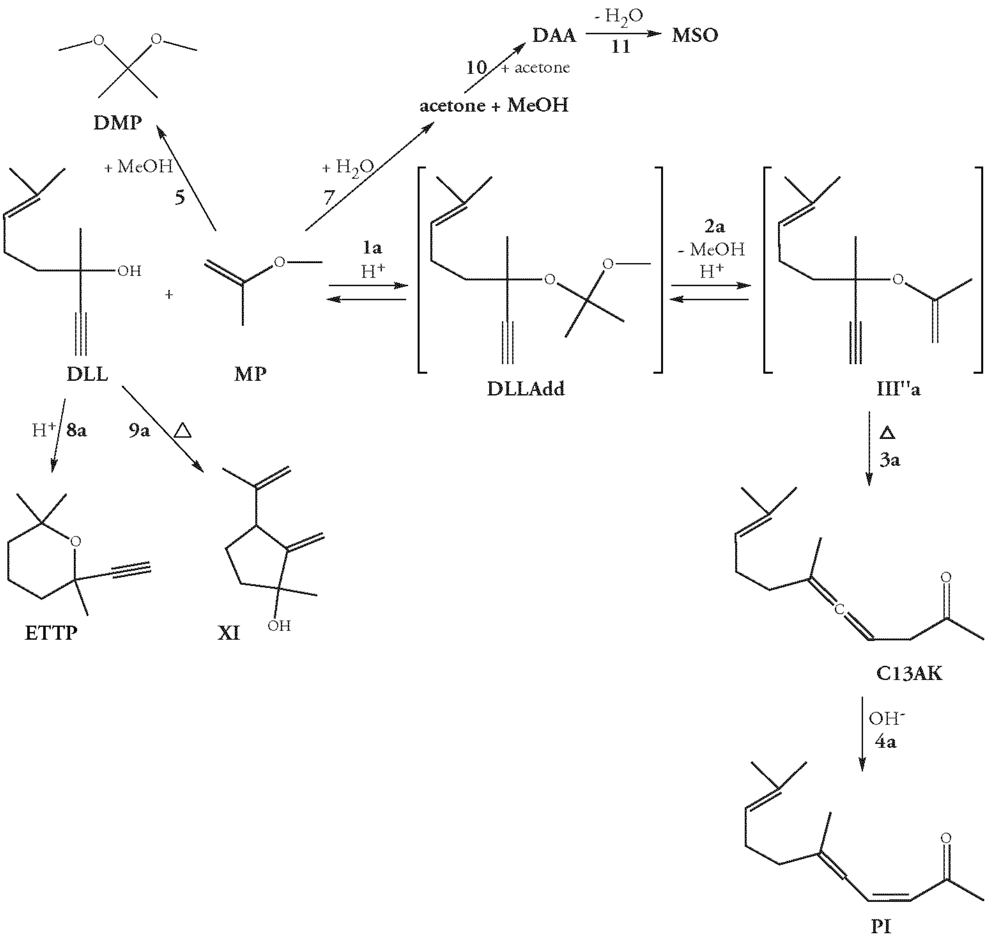

Fig. 3-2: Reaction pathway of dehydrolinalool-ketonization. DLL: dehydrolinalool (3,7-dimethyl-oct-6-en-1-yn-3-ol); MP: 2-methoxypropene; DLLAdd: DLL-MP-addition product (3-(1-methoxy-1-methylethoxy)-3,7-dimethyl-6-octen-1-yne); III"a: 3,7-dimethyl-3-[(1-methylethenyl)oxy]-6-octen-1-yne; C13AK: 6,10-dimethyl-4,5,9-undecatrien-2-one; PI: pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one); DMP: 2,2-dimethoxypropane; MeOH: methanol; ETTP: 2-ethynyltetrahydro-2,6,6-trimethyl-2H-pyran; XI: 1-methyl-2-methylene-3-(1-methylethenyl)-cyclopentanol; DAA: diacetone alcohol (acetone dimer, 4-hydroxy-4-methyl-2-pentanone); MSO: mesityloxide (4-methyl-3-penten-2-one).

(DLL) and 2-methoxypropene (MP) react acid catalyzed to an addition product (DLLAdd). Then, after elimination of methanol (MeOH), which is also acid catalyzed, intermediate product III"a is formed (reaction step 2a). This molecule finally rearranges in a thermal reaction (3a) to the desired product (C13AK). With the use of base catalysts, C13AK would rearrange in a consecutive reaction (4a) to pseudoionone (PI). Starting material DLL can either rearrange acid catalyzed (8a) to ETTP or thermally (9a) to product XI. MP on the other hand forms together with MeOH, eliminated from intermediate product DLLAdd, co-product DMP (reaction 5) or together with water acetone and MeOH (reaction 7). Acetone can dimerize to DAA (reaction 10), which can react further, together with water, to form MSO (reaction 11).

Main focus of this work was to find an adequate solid acid to carry out the DLL-ketonization reaction and to investigate time on stream behaviour of the catalyst and parametric sensitivities. Values for conversion, selectivity and yield were calculated according to the definitions given at the end of Chapter 2.1. Since one DMP-equivalent is automatically formed (as co-product) per C13AK-equivalent (c.f. Figure 3-1), maximum values related to MP for selectivity to C13AK and C13AK-yield are 50 %.

3.2 Catalyst Screening

Before starting thorough examinations of parametric sensitivities on the DLL-ketonization reaction, a series of catalyst screening experiments was carried out to determine, which catalysts show highest conversions and selectivities to the desired product C13AK.

BET-measurements were carried out to determine surface areas and average pore sizes of selected catalysts (c.f. Table 2-2).

Most of the tested samples showed average pore diameters in a mesoporous size range (2 nm-50 nm). Whereas ion exchange catalysts had relatively narrow pore size distributions around the average pore sizes, zeolites showed bimodal distributions of pore sizes, which makes determination of these values for zeolites questionable.

Only Amberlyst 15-, Lewatit SP 112 WS- and Bayer K 2441-samples showed surface areas below 100 m^2 g^{-1}, whereas all the other catalysts exhibited relatively large surface areas.

Table 3-1 gives the corresponding results from catalytic screening experiments. As mentioned before (Chapter 2.2.1), this catalyst screening was carried out with a sample technique, which was inappropriate for experiments with large differences of viscosities between samples before and after reaction. However, as repeated experiments with the more precise sampling technique indicated, qualitative interpretation of the results was still valid.

Table 3-1: Results from catalyst screening. Conditions: 4 g of untreated catalyst, 110 °C, 10 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 m DLL min^{-1}, samples taken after 4 h of constant conditions.

Catalyst	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$ [%]	$S_{C13AK, DLL}$ [%]	$S_{ETTP, DLL}$ [%]	$Y_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]
Deloxan ASP I/9	47.0	21.7	14.7	82.9	0.0	6.9	18.0
sulfated and TiO_2-modified amorphous SiO_2	77.7	30.3	18.2	59.7	0.0	14.1	18.1
Zeocat PB/H	95.6	8.1	3.0	89.3	0.0	2.9	7.2
NaHY	73.0	2.3	1.1	99.9	0.0	0.8	2.3
Lewatit S 2328	96.2	63.0	0.4	1.7	32.4	0.4	1.1
Amberlyst 15 Dry	96.8	48.8	0.3	1.8	33.4	0.3	0.9
Zeocat PZ-2/100H	39.0	10.6	0.5	4.1	0.0	0.2	0.4
Lewatit SP 112 WS	0.5	6.8	18.0	4.0	0.0	0.1	0.3

Table 2-1 in Chapter 2.5 shows a complete list of all the tested catalysts. Those catalysts listed, but not discussed in the current chapter, did not prove to be useful catalysts for synthesis of the desired product.

Experiments with various Nafion catalysts are also described in more detail in the Appendix.

The catalyst screening experiments were carried out at “standard conditions” (see Chapter 2.1) (exception: pressure of 10 bar instead of 50 bar) and the catalysts were used as received (without washing with ethanol or 40 h conditioning). As described later (Chapter 3.5.2), the difference in pressure from standard pressure did not influence the decision significantly whether a catalyst is efficient for C13AK synthesis or not, due to the weak influence of pressure.

In Table 3-1 results for Bayer K 2441 and Zeocat FM-8/25H are missing. By using Bayer K 2441 a high temperature rise just after starting to pump the reactants to the system occurred. Even by reducing the flow to standard flow conditions the rapid temperature increase could not be stopped, which would have been harmful for the system, if the experiment were not terminated. The product stream consisted of dark, viscous polymeric substances and almost all of the pumped MP was consumed (conversion of 99 %).

In the experiment with Zeocat FM-8/25H a very low DLL-conversion (< 0.5 %) could be detected whereas almost no C13AK has been formed. So determination of selectivities was not reasonable, because sampling was prone to errors at these low concentrations.

Most important criterion for evaluation of a suitable catalyst for DLL-ketonization was the yield of C13AK related to DLL. Considering this factor, results in Table 3-1 show two catalysts, which fulfil that requirement significantly better (yields of 18 %) than all the others (yields between 0.3 and 7 %): Deloxan ASP I/9 and sulfated and TiO_2-modified amorphous SiO_2. Only the two aforementioned catalysts show a combination of acceptable selectivity and a DLL-conversion of higher than 20 % and are thus suitable for the DLL-ketonization reaction.

In general, all of the tested catalysts (except Lewatit SP 112 WS) were acidic enough to accelerate reactions with MP. DLL-conversions were lower than MP-conversions (except with Lewatit SP 112 WS) but resulted in a higher selectivity to C13AK related to DLL than to MP.

Most of the tested catalysts showed either high conversion and low selectivity or low (DLL-)conversion and higher selectivity (only exceptions: Deloxan ASP I/9 and sulfated and TiO_2-modified amorphous SiO_2).

Only with two of the observed catalysts, formation of ETTP (formed by acid catalyzed rearrangement of dehydrolinalool, reaction 8a in Figure 3-2) could be detected (Lewatit S 2328 and Amberlyst 15 Dry). Although, for reasonable ETTP synthesis, these catalysts are not selective enough, either (selectivities of 33 % related to DLL).

Generally, increasing average pore diameter of the tested catalysts led to an increase in DLL-conversion (exception: Lewatit SP 112 WS) and a decrease in selectivity to C13AK (related to DLL) (exception: Zeocat PB/H). With increasing pore sizes, relatively large DLL-molecules gain access to a greater fraction of surface area of the catalyst and not only to the outer catalyst shell.

These comparisons were interesting to draw, but for more detailed explanations, two other important factors were missing, which could not be determined with methods used in this work: distribution and amount of active (acidic) sites.

For further investigations decision had to be taken, which catalyst should be chosen to proceed with. Although sulfated and TiO_2-modified amorphous SiO_2 showed about the same results as tests with Deloxan ASP I/9, choice fell to the latter. More constant bead sizes and uniform shapes were the determining factors for Deloxan ASP I/9. The larger bead sizes and less uniform shapes of the silica catalyst would have been more prone to problems with difficult to predict flow phenomenons (channelling, ratio of bead size/reactor diameter etc.).

3.3 Observed Reaction Products and Reaction Pathways

Gas chromatographic analysis of product stream mixtures of the catalyst screening tests revealed various products besides the desired C13AK. In addition to C13AK and ETTP, also MP-dimer (MPD), DLL-MP-addition product (DLLAdd), small fractions of pseudoionone isomers (PI) and of course DMP, which is formed by reaction of MP and methanol (MeOH), were identified (c.f. Figure 3-2). Whereas formation of MPD leads to undesired reactant loss and lower selectivity, DLLAdd can react further (in a consecutive thermal reaction (2a+3a)) to C13AK, the desired product. In industrial processes, produced DMP is normally recycled to its starting materials (MP and MeOH), but in this work, it was an unavoidable co-product of the ketonization reaction. MeOH and acetone were also found in the product mixture (reaction 7). Products XI, DAA, MSO and III"a (unstable, reacted immediately further to C13AK at reaction conditions used) (c.f. Figure 3-2) could not be observed in the reaction products from any experiments. Many other different products were detected by GC-analysis in certain samples, but all of these were only observable in small fractions, which either made identification impossible or extremely demanding. Product streams of experiments with high conversion rates and low selectivities often contained dark, oily solids that most probably consisted of polymeric compounds that could not be detected by GC-analysis. But main products were those described in more detail earlier.

As in the experiments from the catalyst screening program, in the time on stream experiment and parametric sensitivities experiments, mainly C13AK and DMP could be observed as reaction products, whereas DLLAdd, ETTP, MPD, MeOH, acetone and PI on the other hand were the most often occurring intermediate-, side- resp. consecutive-products in the product mixtures (cf. Figure 3-2). Water, which was not detectable in GC-analysis, caused formation of acetone and MeOH (reaction 7). Increase of MeOH-content in the system, as a consequence, resulted in larger DMP amounts (reaction 5). Thus, water contents in the system had to be kept as low as possible.

Other substances were only detected in traces, in some rare experiments, polymeric products (visible as dark solids in the product stream) were formed at high temperature, but could not be detected by GC-Analysis.

Based on the observed reaction products, the reaction pathways in Figure 3-3 can be postulated.

3.4 Time on Stream Behaviour

A longterm experiment with 9.4 g Deloxan ASP I/9 as catalyst was carried out to investigate time on stream behaviour. After starting a standard experiment (with exception of larger amount of catalyst) samples were taken every few hours.

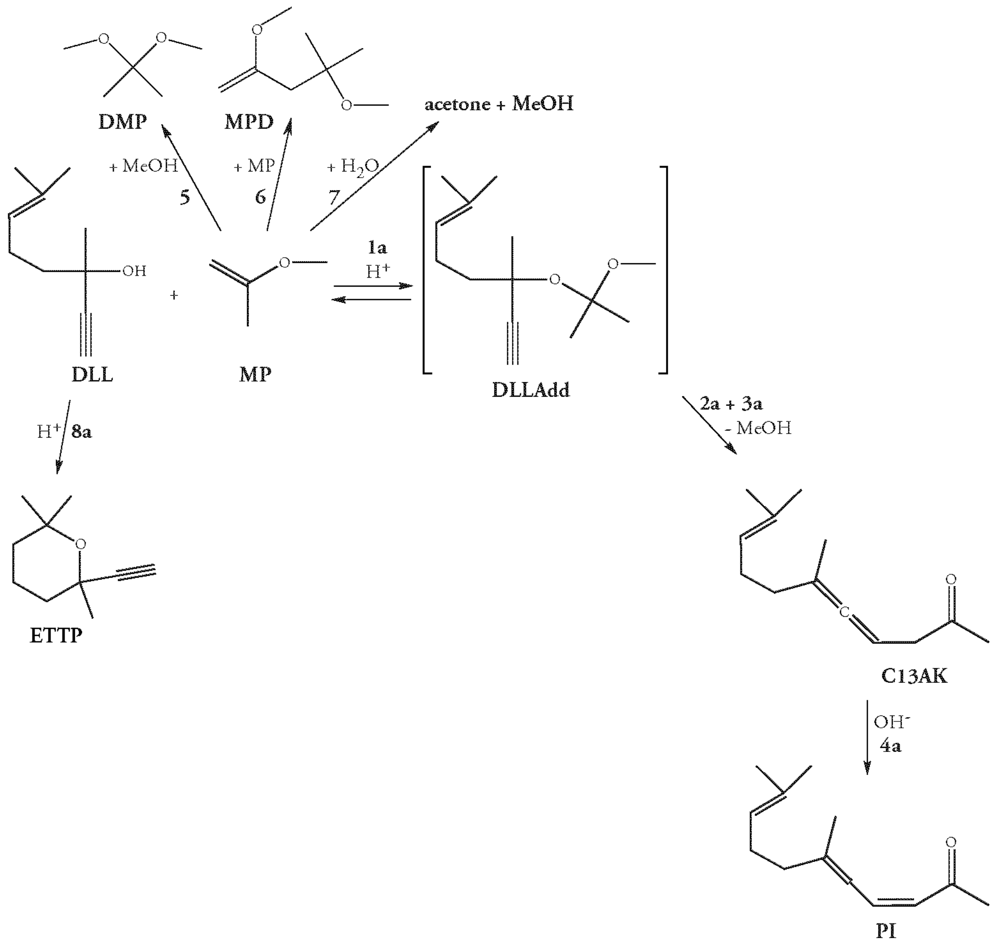

Fig. 3-3: Observed reaction products and postulated reaction pathways. DLL: dehydrolinalool (3,7-dimethyl-oct-6-en-1-yn-3-ol); MP: 2-methoxypropene; DLLAdd: DLL-MP-addition product (3-(1-methoxy-1-methylethoxy)-3,7-dimethyl-6-octen-1-yne); C13AK: 6,10-dimethyl-4,5,9-undecatrien-2-one; PI: pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one); DMP: 2,2-dimethoxypropane; MPD: 2-methoxypropene dimer (MP-dimer; 2,4-dimethoxy-4-methyl-1-pentene); MeOH: methanol; ETTP: 2-ethynyltetrahydro-2,6,6-trimethyl-2H-pyran.

Behaviour related to DLL

As emerges from Figure 3-4, DLL-conversion started at about 47 % and then reached a nearly constant level at about 55 %. A similar behaviour could be observed for selectivity to C13AK. Selectivity increased with time to a constant level at about 96 %. Thus after the initial period yield of C13AK remained at a constant level.

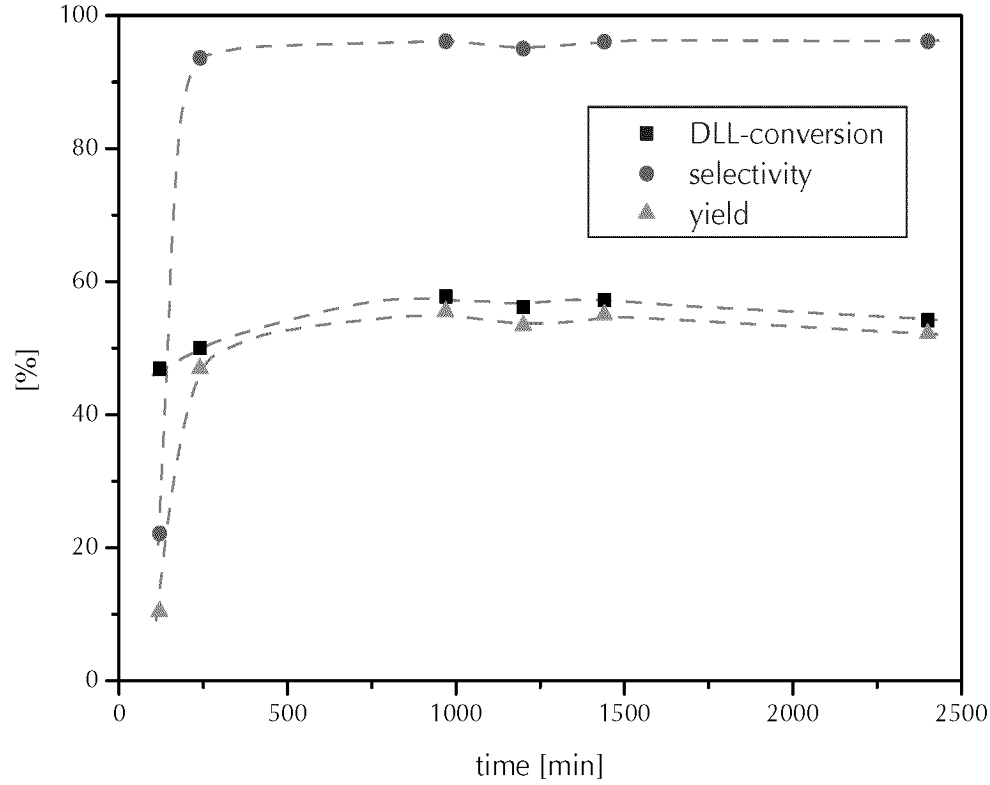

Fig. 3-4: Time on stream experiment; DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL) vs. time. Conditions: 110 °C, 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 9.4 g Deloxan ASP I/9 catalyst. Dashed lines are drawn as a guide for the eyes.

Behaviour related to MP

Figure 3-5 shows the time on stream behaviour related to MP. MP-conversion started at about 96 % and continuously decreased with time. In contrast to DLL-conversion no constant conversion was observed during 2400 min measuring time. Selectivity to C13AK related to MP increased with time on stream and reached a maximum of about 30 % after 40 h. Note that the maximal selectivity to the allene ketone C13AK is 50 % when related to MP consumption. Yield of C13AK related to MP showed a similar behaviour as yield related to DLL. After a short induction period it reached an almost constant level of about 20 %.

The main conclusion that could be drawn from the time on stream experiment was that a catalyst conditioning of at least 30 h was necessary to condition the catalyst to a certain constant performance level, before fractions of it

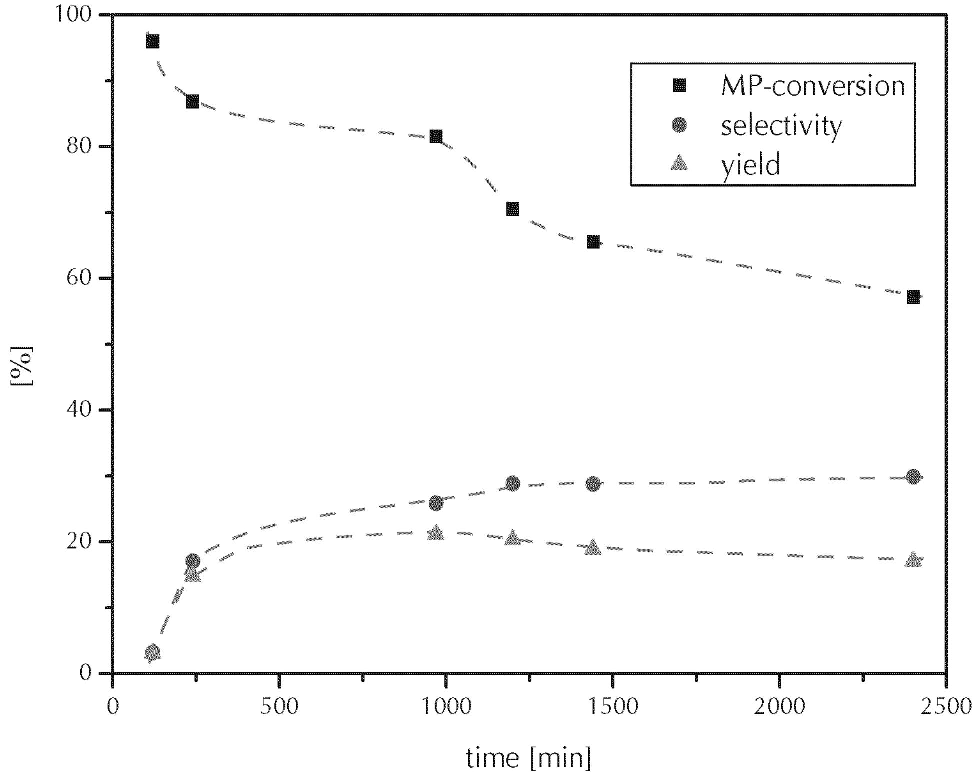

Fig. 3-5: Time on stream experiment; MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP) vs. time. Conditions: 110 °C, 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 9.4 g Deloxan ASP I/9 catalyst. Dashed lines are drawn as a guide for the eyes.

were usable in parametric sensitivity studies. After this relatively long time on stream, the catalyst still showed good performance values (especially selectivity to the desired product related to reacted DLL).

3.5 Parametric Sensitivity

To evaluate catalytically important parameters, a parametric sensitivity study for DLL-ketonization was carried out. In every experiment one single parameter was varied, while all other parameters were kept constant (compare with Chapter 2.1).

3.5.1 Temperature

Figure 3-6 and Figure 3-7 depict the temperature dependence of the main parameters characterizing the catalytic behaviour.

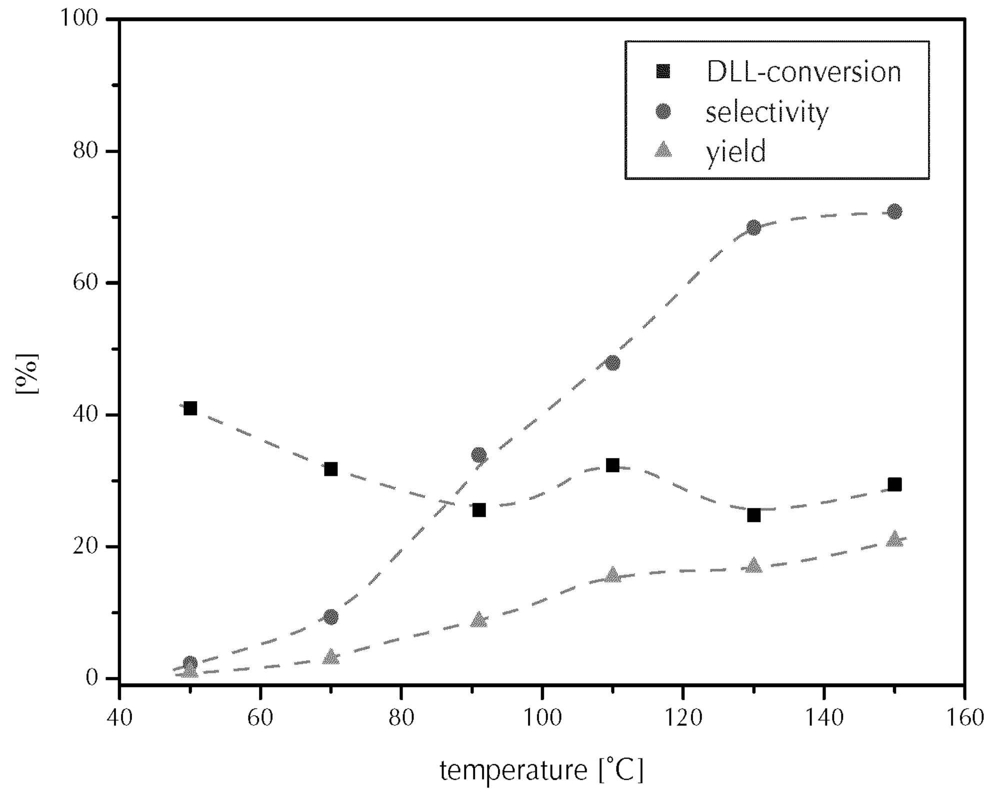

Fig. 3-6: Influence of temperature on DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL). Conditions: 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

Behaviour related to DLL

DLL-conversion slightly decreased with increasing temperature. This weak dependence is attributed to the fact that the exothermic reaction of DLL and MP to form DLLAdd is probably close to equilibrium, and the equilibrium is shifted towards reactants with increasing temperature.

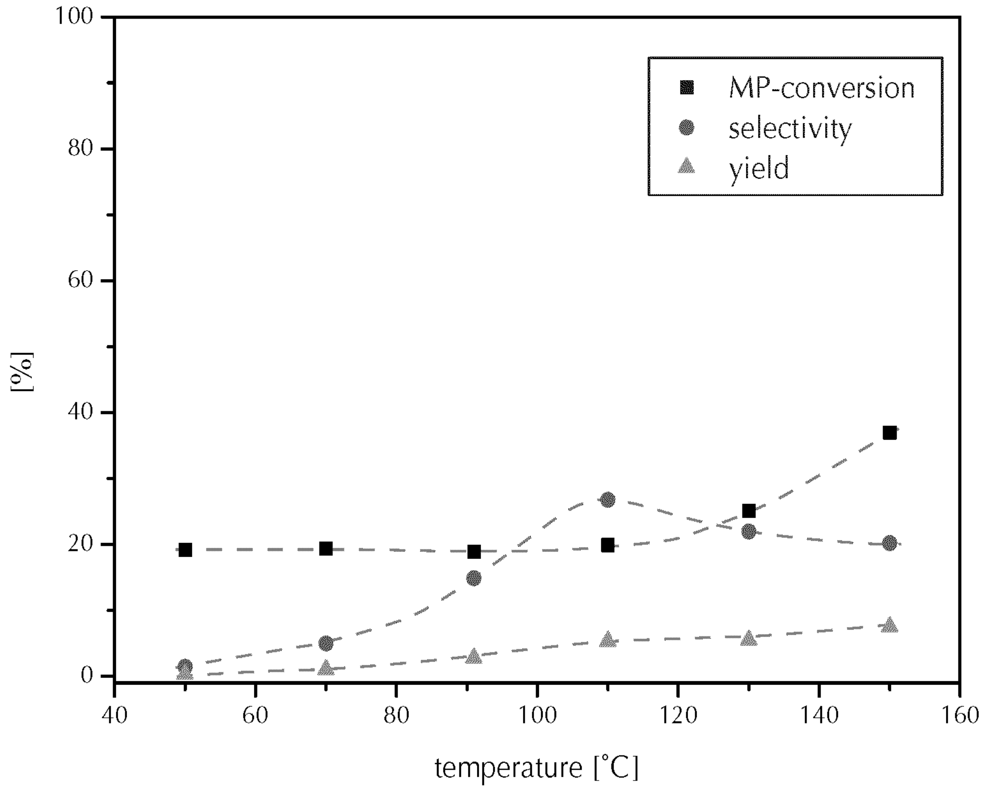

Fig. 3-7: Influence of temperature on MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP). Conditions: 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

At low temperature almost no desired product formed (selectivity below 10 %). The reaction virtually stopped at the DLLAdd intermediate (reaction 1a), which by thermal rearrangement yields C13AK (reaction 2a and 3a). Temperature required to activate this rearrangement step was apparently not high enough below 90 °C. Above ca. 90 °C, almost no DLL-MPAdd could be detected in the product stream leaving the reactor, which means that nearly all intermediate product thermally rearranged to the desired C13AK. Thus, selectivity increased continuously at higher temperature.

Concerning yields of C13AK, with rising temperature yield related to DLL continuously increased. Due to technical limitations (sensitivity of some equipment to high temperature) no experiments could be carried out at possibly more interesting higher temperature. It could be speculated that at even higher temperature conversion would rise, but on the other hand, selectivity would decrease, due to more favoured side reactions at higher temperature (formation of polymeric compounds).

Behaviour related to MP

MP-conversion, in contrast to DLL-conversion, continuously increased above ca. 110 °C. In contrast, the various side reactions (reactions 5, 6 and 7, Figure 3-3) occurring with MP seem not to be thermodynamically controlled and consequently MP-conversion is strongly affected by the kinetics of the side reactions. MP-reactions 5, 6 and 7 were favoured at lower temperature compared to MP-reactions with DLL (reaction 1a).

Selectivity to C13AK related to MP increased steadily up to ca. 110 °C and then slightly declined due to occurring side reactions (reactions 5, 6, 7 and formation of polymeric compounds).

3.5.2 Pressure

From the experiments in which the influence of pressure was investigated, we can conclude that pressure only weakly affects reaction behaviour (cf. Figure 3-8 and Figure 3-9).

Behaviour related to DLL

Neither conversion, selectivity nor yield related to DLL changed dramatically in dependence of pressure. Over a pressure range of almost 90 bar, yield to C13AK varied only by about 1 %.

Behaviour related to MP

The same behaviour could be observed related to MP. Neither conversion, selectivity nor yield changed remarkably. However, at pressures below 6 bar (at 110 °C), the change of the lower boiling reactant (MP; b.p. 34 °C) from liquid to gas phase affected the reaction behaviour. Since gas phase reactions of MP (reactions 5, 6, 7 and others) were much faster than reactions in the liquid phase (desired reaction 1a with liquid DLL), selectivity to C13AK dropped immediately.

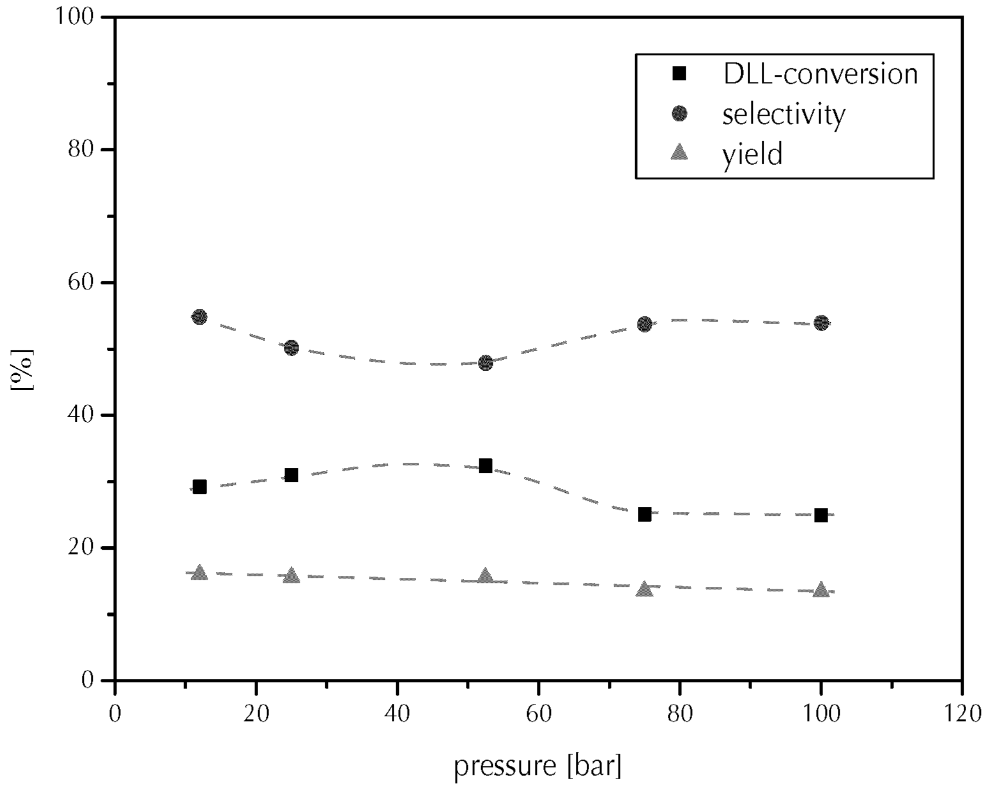

Fig. 3-8: Influence of pressure on DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL). Conditions: 110 °C, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

3.5.3 Total Flow

While keeping the molar reactant ratio MP/DLL at about three, total liquid flow was varied from 0.3 ml min^{-1} (lower flow limit of HPLC-pump for DLL ca. 0.1 ml min^{-1}) to 1.5 ml min^{-1}. In terms of liquid hourly space velocities this corresponds to a change from 2.4 to 12.0 h^{-1}.

Figure 3-10 and Figure 3-11 show the catalytic behaviour resulting from this change of total flow rate.

Behaviour related to DLL

As expected, conversion related to DLL increased with decreasing flow rate (increasing residence time in the reactor).

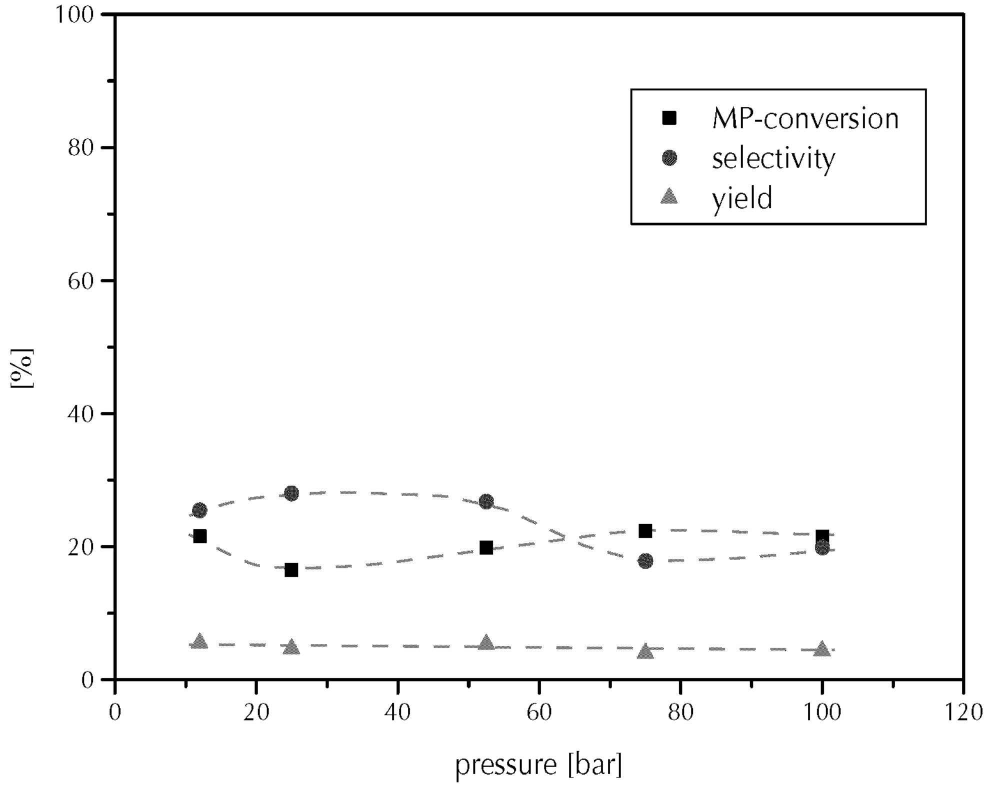

Fig. 3-9: Influence of pressure on MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP). Conditions: 110 °C, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

On the other hand, selectivity to the desired product C13AK decreased with decreasing liquid flow. Apparently longer residence time favoured formation of side products (reaction 5, 6 and 7).

This decrease in selectivity was not strong and consequently higher conversion was accompanied by a slow but continuous increase in yield.

Behaviour related to MP

A different dependence could be observed for the reaction performance related to MP. Conversion decreased with increasing flow rate, whereas selectivity remained at an almost constant level (maximum at a flow rate of about 0.6 ml min^{-1}) and consequently yield slightly decreased with increasing flow.

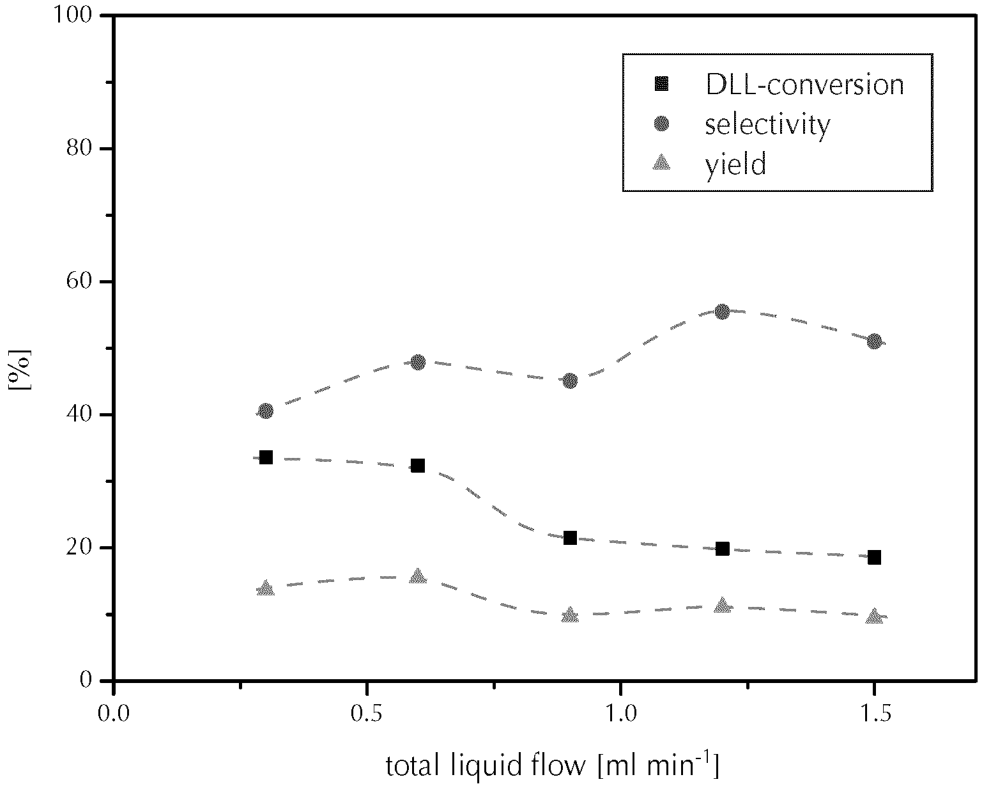

Fig. 3-10: Influence of flow rate on DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL). Conditions: 110 °C, 50 bar, molar ratio MP/DLL=3, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

At the lowest flow rate (0.3 ml min^{-1}), side reactions 5, 6 and 7 seemed to be favoured resulting in a significantly lower selectivity to the C13AK product.

3.5.4 Molar Ratio

In Figure 3-12 and Figure 3-13 results from experiments with different molar reactant ratios of MP/DLL at a constant total flow rate of 0.6 ml min^{-1} are shown. Note that from a stoichiometrical point of view, a molar ratio of two would be optimal for the reaction of DLL and MP to produce C13AK and the co-product DMP (Figure 3-1).

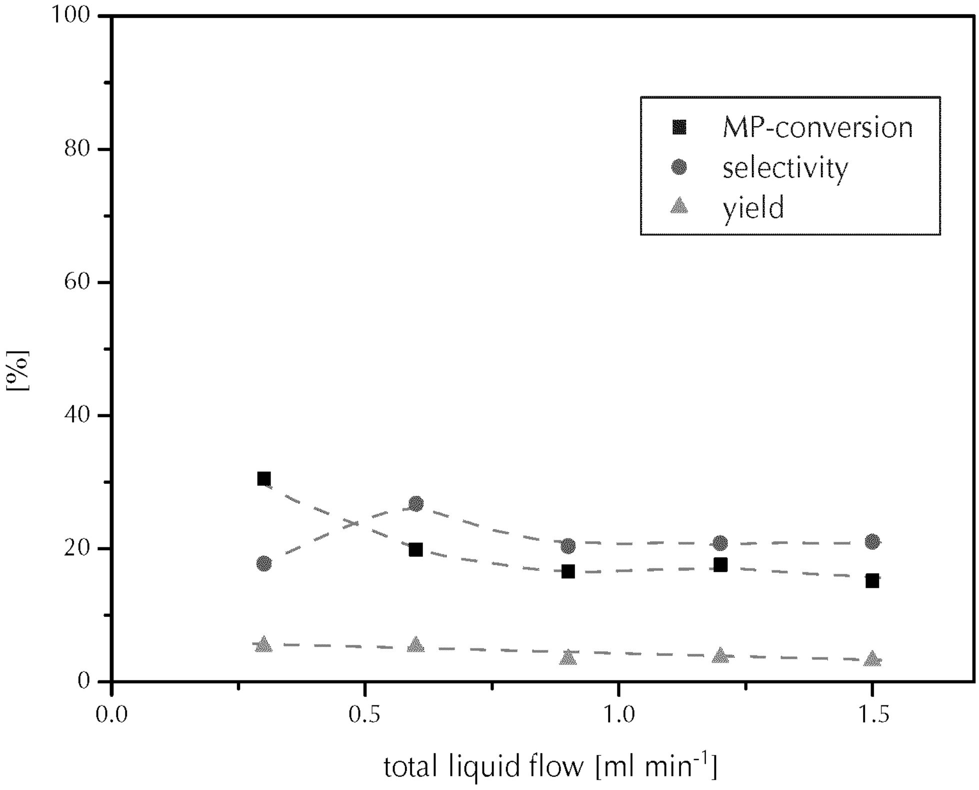

Fig. 3-11: Influence of flow rate on MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP). Conditions: 110 °C, 50 bar, molar ratio MP/DLL=3, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

Behaviour related to DLL

Related to DLL conversion and selectivity to C13AK showed opposite tendencies. At low MP/DLL ratio conversion was low, whereas selectivity to C13AK was high. DLL-conversion increased and reached a constant level of about 30 % with increasing molar ratio MP/DLL, whereas selectivity to C13AK decreased continuously. This behaviour accounts for a weak dependence of yield on the molar ratio of reactants.

Behaviour related to MP

At low molar ratios of MP/DLL, MP reacted more selectively with DLL than at higher molar ratios which is attributed to the lower probability of side reactions between MP-molecules (e.g. reaction 6). At higher MP/DLL ratios undesired side reactions (5, 6 and 7) are favoured. Increasing the amount of MP in

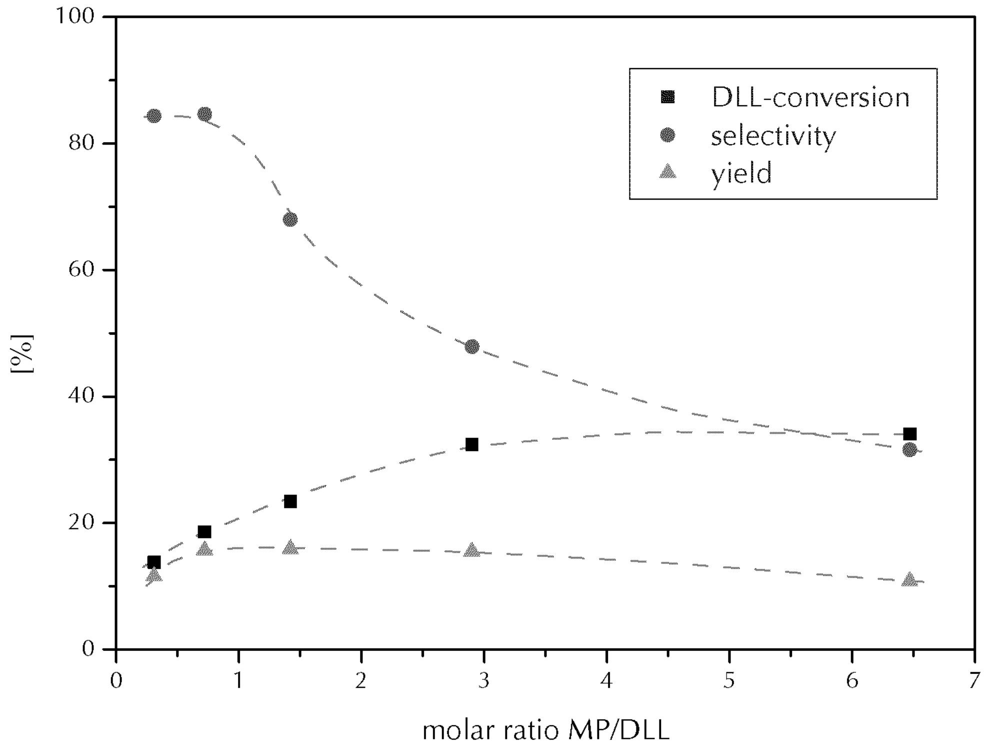

Fig. 3-12: Influence of molar ratio (MP/DLL) on DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL). Conditions: 110 °C, 50 bar, total flow rate: 0.6 ml min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

the feed stream resulted in lower MP-conversion, as expected. As a consequence, lowering the molar ratio of MP/DLL afforded higher yield of C13AK related to MP.

3.5.5 Pretreatment

Preceding experiments with solid acids showed considerable effects of pretreatment of the catalyst on catalytic results. Therefore, pretreatment studies with three different agents were carried out.

After 40 h of catalyst conditioning at standard conditions, fractions of 4 g of catalyst were normally used to carry out the parametric sensitivity experiments. Catalyst fractions for experiments in this chapter were (after longterm conditioning) additionally pretreated in situ, before a standard experiment was started. MP, DLL resp. MeOH were pumped through the reactor during expe-

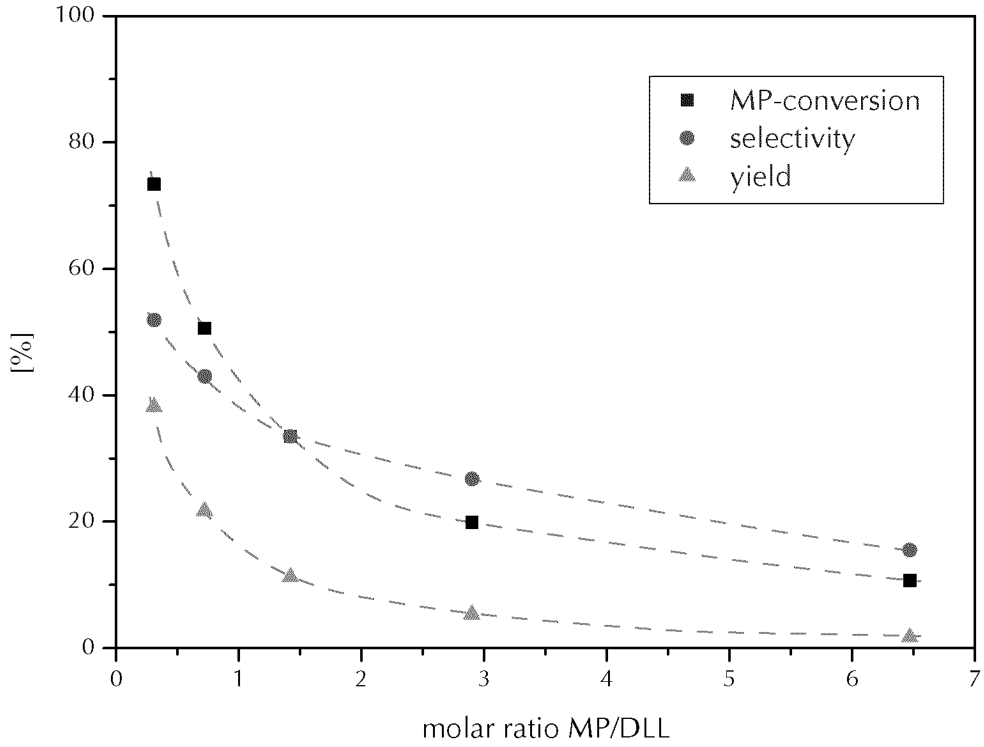

Fig. 3-13: Influence of molar ratio (MP/DLL) on MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP). Conditions: 110 °C, 50 bar, total flow rate: 0.6 ml min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions). Dashed lines are drawn as a guide for the eyes.

riment start-up procedure and for another 30 min at standard conditions. Figure 3-14 and Figure 3-15 present a comparison of the results with untreated catalyst (only standard conditioning of 40 h).

Behaviour related to DLL

The catalyst treated with MP showed a higher selectivity to C13AK related to DLL, but led to a lower conversion than the untreated catalyst. This behaviour resulted in almost equal yields.

For the pretreatment with DLL, the following could be observed: all of the performance values (X, S and Y) were almost exactly the same as for results with untreated catalyst. Hence, pretreatment with DLL had no significant influence on catalytic results.

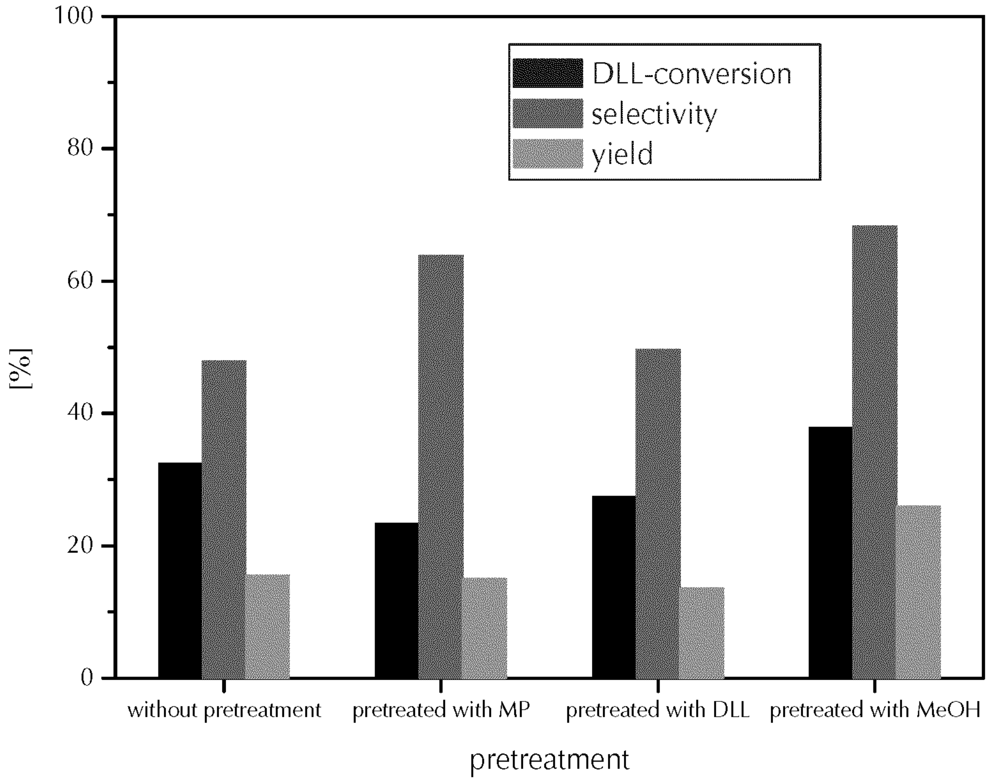

Fig. 3-14: Influence of catalyst pretreatment on DLL-conversion, selectivity to C13AK (related to DLL) and yield of C13AK (related to DLL). Conditions: 110 °C. 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions), pretreatment with indicated substance for 30 min (3 ml min^{-1}) at reaction conditions.

Finally pretreatment with MeOH was studied. Here, all values related to DLL (X, S and Y) increased compared to an experiment with untreated catalyst. A selectivity increase of 20 % (from 48 to 68 %) could be observed.

Behaviour related to MP

For values related to MP, selectivity of MP-pretreated catalyst was lower as selectivity of untreated catalyst. Since conversions behaved contrarily, also here yield remained at the same level.

As for behaviour related to DLL, pretreatment with DLL had no influence on results related to MP compared to untreated catalyst.

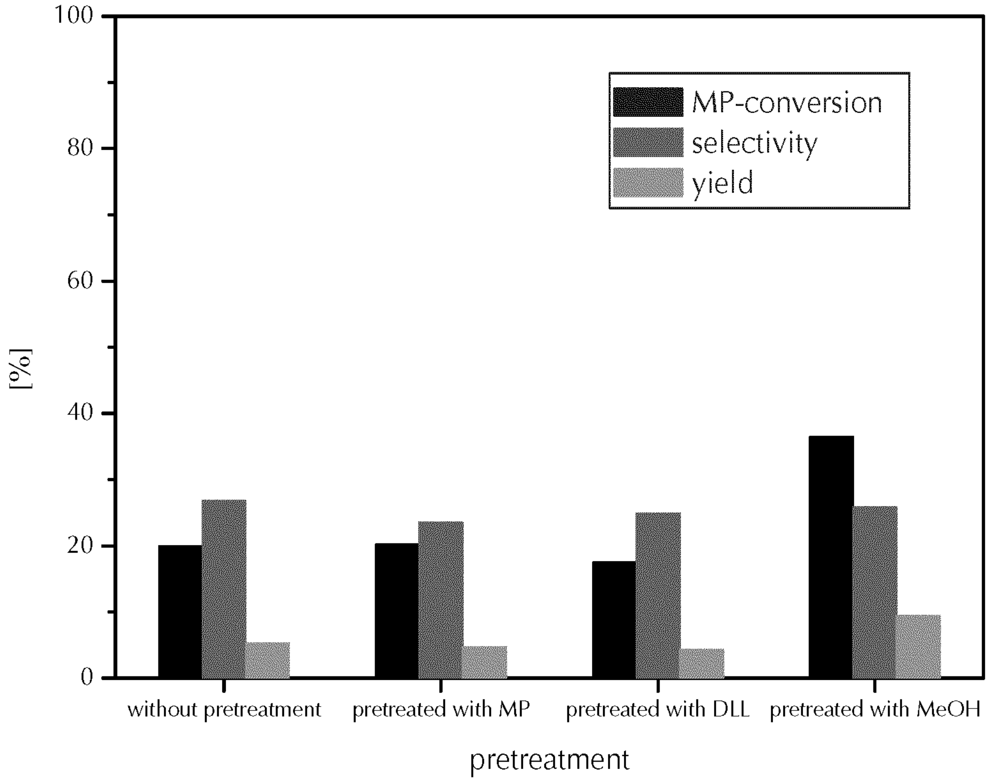

Fig. 3-15: Influence of catalyst pretreatment on MP-conversion, selectivity to C13AK (related to MP) and yield of C13AK (related to MP). Conditions: 110 °C. 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 40 h at reaction conditions), pretreatment with indicated substance for 30 min (3 ml min^{-1}) at reaction conditions.

Related to MP, MeOH pretreatment resulted in a slightly lower selectivity, but conversion increased from 20 to 36.5 %, which resulted in a yield improvement of about 4 % compared to untreated catalyst.

From the pretreatment agents used (MP, DLL and MeOH) only MeOH showed advantages concerning yield compared to the experiment without pretreatment. Probably MeOH, due to its dissolving power, eliminated contaminants from the catalyst surface. The relatively long experiment time of 4 h after pretreatment possibly resulted in recontamination and/or restructuring of the formerly pretreated surface.

3.6 Conclusions

The heterogeneously catalyzed ketonization reaction of dehydrolinalool and 2-methoxypropene was carried out in a continuous flow reactor system. Screening of more than 30 potential commercial catalysts indicated that the most powerful catalyst is an alkyl sulfonic acid polysiloxane from Degussa: Deloxan ASP I/9. Only sulfated and TiO_2-modified amorphous SiO_2 showed a comparable performance. With most of the other catalysts only unselective reactions (mostly formation of polymeric compounds) could be observed or conversions of the two reactants were too low for reasonable application.

Time on stream behaviour of the most suitable catalyst (Deloxan ASP I/9) was tested and even after 40 h of use, catalytic results were still at relatively high levels and constant. C13AK-yields of up to 54 % related to DLL were achieved (with a DLL-conversion of about 57 % and a selectivity to C13AK (related to DLL) of about 95 %). Before use in the parametric sensitivity experiments, catalyst samples were conditioned at standard reaction conditions for 40 h.

Parametric sensitivity studies showed the influences of temperature, pressure, total liquid flow, molar ratio MP/DLL and catalyst pretreatment (consisting of exposure to MP, DLL resp. MeOH at reaction conditions).

As regards selectivity to C13AK, higher temperatures seem favourable because they are necessary for the rearrangement step in the main reaction pathway.

Pressure was found to have a minor influence on the catalytic performance.

In the range investigated, the flow rate also exhibited a relatively weak influence on the catalytic performance. Low flow rate favoured some side reactions of MP leading to lower selectivity to C13AK related to MP, whereas conversion increased, as expected.

Changes of the molar ratio MP/DLL influenced catalytic results as follows: related to DLL, a maximum C13AK-yield could be observed at a MP/DLL ratio of about 1.5, whereas yield related to MP continuously decreased with increasing MP/DLL ratio, as a consequence of enhanced side reactions of MP.

Finally, a catalyst pretreatment with MP, DLL resp. MeOH showed that (compared to untreated catalyst) only MeOH pretreatment improved catalytic performance (due to its dissolving properties). The other two pretreatment agents caused formation of undesired catalyst contaminants, which even lowered catalyst activity.

Reaction products observed in these studies corresponded to those postulated in literature: Besides the desired ketone (C13AK) also co-product DMP, DLL-MP-addition product (DLLAdd), DLL-rearrangement product (ETTP), MeOH, acetone and traces of pseudoionone (PI) were found. Additionally, also formation of MP-dimer (MPD) and polymeric compounds were observed.

The applicability of a solid acid catalyst was proven, although yields achieved with liquid catalysts still lie at higher levels (comparison, however, is difficult to draw, because in published studies, experiments were carried out in batch reactor systems).

Chapter 4

2-Methyl-3-butyn-2-ol-Ketonization in Continuous Flow Reactor System

4.1 Introduction

In order to test how a reactant with a shorter chain-length behaves, 2-methyl-3-butyn-2-ol (MB) instead of DLL was used in a similar Saucy-Marbet ketonization reaction. Differences in the reaction behaviour compared to DLL-ketonization should be elucidated. Figure 4-1 shows the corresponding reaction scheme of 6-methyl-4,5-heptadien-2-one (C8AK) synthesis.

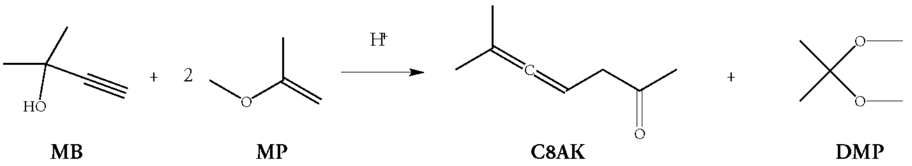

Fig. 4-1: Reaction scheme of 2-methyl-3-butyn-2-ol-ketonization.

Homogeneously catalyzed batch reactor MB-ketonization studies have been carried out in the past, whose C8AK-yields (related to MB) reached values of up to 95 % (with reaction times of up to 24 h) [2, 6].

In Figure 4-2 a more detailed view of the reaction pathway, as indicated in literature [2, 4, 45-47, 144, 145], is presented.

The starting reactants 2-methyl-3-butyn-2-ol (MB) and 2-methoxypropene (MP) react acid catalyzed to an addition product MBAdd (reaction 1b), which then reacts further to product III"b (this elimination of MeOH (reaction 2b) is also acid catalyzed). Intermediate product III"b finally rearranges in

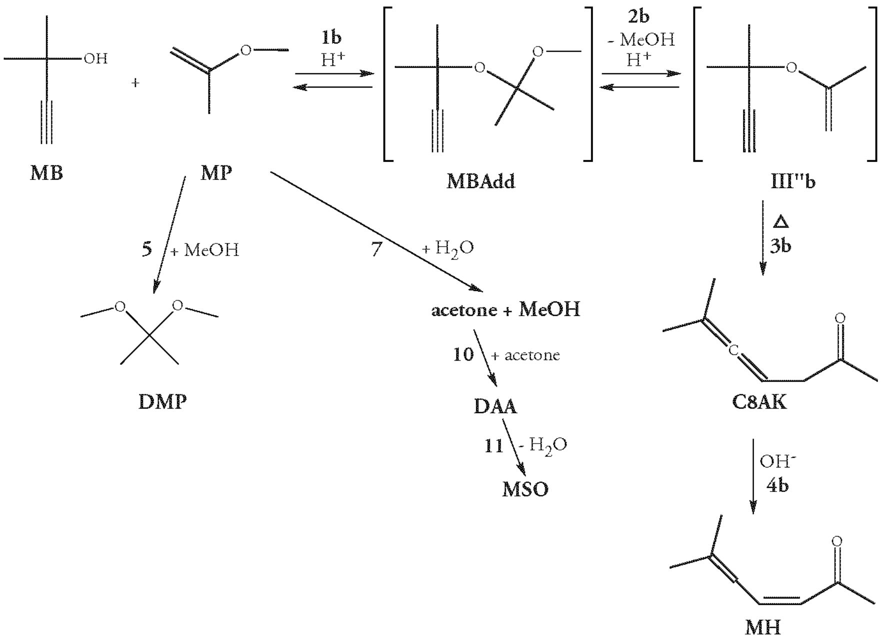

Fig. 4-2: Reaction pathway of 2-methyl-3-butyn-2-ol-ketonization. MB: 2-methyl-3-butyn-2-ol; MP: 2-methoxypropene; MBAdd: MB-MP-addition product (3-(1-methoxy-1-methylethoxy)-3-methyl-1-butyne); III"b: 3-methyl-3-[(1-methylethenyl)oxy]-1-butyne; C8AK: 6-methyl-4,5-heptadien-2-one; MH: 6-methyl-3,5-heptadien-2-one; DMP: 2,2-dimethoxypropane; MeOH: methanol; DAA: diacetone alcohol (acetone dimer, 4-hydroxy-4-methyl-2-pentanone); MSO: mesityloxide (4-methyl-3-penten-2-one).

a thermal reaction (3b) to the desired product C8AK, which, in a basic environment, can form product MH (reaction 4b). Starting compound MP forms together with MeOH, which is eliminated from MBAdd during reaction 2b, co-product DMP (reaction 5), dimerizes to product MPD (reaction 6) or forms together with water acetone and MeOH (reaction 7). Formed acetone can dimerize to DAA (reaction 10), which can further react to MSO (reaction 11).

As for DLL-ketonization, time on stream behaviour and parametric sensitivity were investigated. Conversion, selectivity and yield were calculated as defined at the end of Chapter 2.1. C8AK-yields and selectivities related to MP can only reach a maximum of 50 % (due to unavoidable formation of co-product DMP (c.f. Figure 4-1)).

4.2 Observed Reaction Products and Reaction Pathways

In all experiments with 2-methyl-3-butyn-2-ol (MB), C8AK and DMP were formed as main products beside MBAdd and MPD which also were detected in substantial amounts in the product stream. MBAdd is an intermediate product (formed by reaction 1b) in C8AK-synthesis which can further react to the desired product (reactions 2b and 3b). MP that dimerized to MPD (reaction 6), on the other hand, is excluded from the desired reaction pathway. Numerous other by-products were observed, but all only in small amounts, thus only a few could be identified (e.g. DAA, MSO, IP, MeOH, acetone, MH). Product III"b could not be detected in these experiments (the intermediate product probably immediately reacted further to C8AK at the used reaction conditions (reaction 3b)). As in DLL-ketonization at higher temperatures, dark oily solids were visible in the product mixture. Most probably also water was present in the system (since it is necessary for observed reactions 7 and 11), but could not be detected by GC-analysis.

The observed products and their postulated corresponding reaction pathways for the MB-ketonization are presented in Figure 4-3.

4.3 Time on Stream Behaviour

An experiment with 9.4 g of untreated Deloxan ASP I/9 catalyst (only washed and dried as described in Chapter 2.5) was carried out to determine the time on stream behaviour of the catalytic reaction. Results compiled in Figure 4-4 and Figure 4-5 show that the catalyst started production of the desired C8AK only after an activation time of about 1000 min. In the initial period only undesired reactions occurred (mainly reactions 5 and 7). During this period, the reactant conversion increased until a maximum was reached after about 810 min.

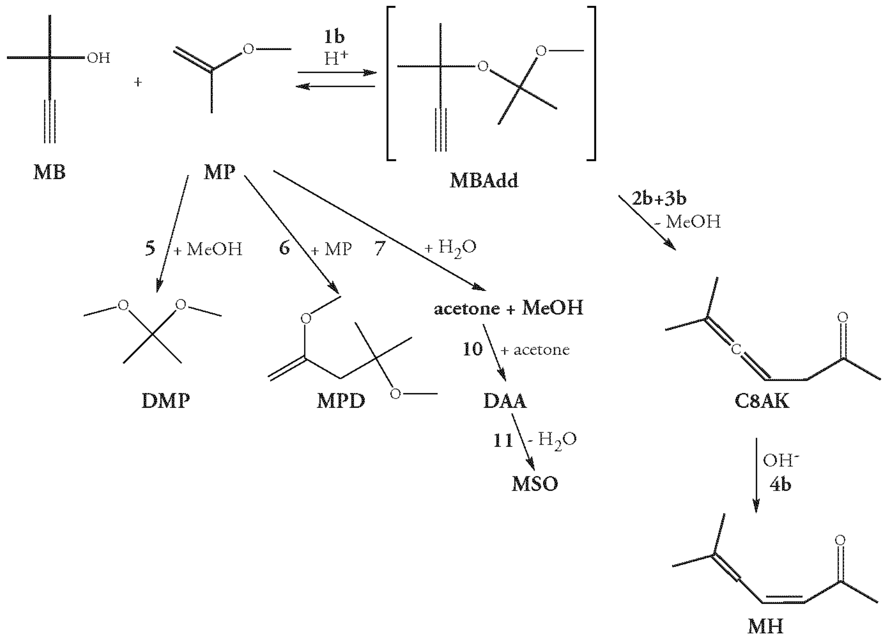

Fig. 4-3: Observed reaction products and postulated reaction pathways. MB: 2-methyl-3-butyn-2-ol; MP: 2-methoxypropene; MBAdd: MB-MP-addition product (3-(1-methoxy-1-methylethoxy)-3-methyl-1-butyne); C8AK: 6-methyl-4,5-heptadien-2-one; MH: 6-methyl-3,5-heptadien-2-one; DMP: 2,2-dimethoxypropane; MPD: 2-methoxypropene dimer (MP-dimer; 2,4-dimethoxy-4-methyl-1-pentene); MeOH: methanol.

Behaviour related to MB

Although conversion remained at an almost constant level after about 500 min on stream, selectivity to C8AK still increased after more than 1200 min (Figure 4-4).

Behaviour related to MP

Compared to the behaviour related to MB nearly constant conversion and selectivity could only be observed after more than 1440 min on stream, indicating that steady-state with respect to MP related performance parameters was much more slowly attained.

From that point of view, a conditioning time for Deloxan ASP I/9 of 24 h was chosen for the following parametric sensitivity experiments.

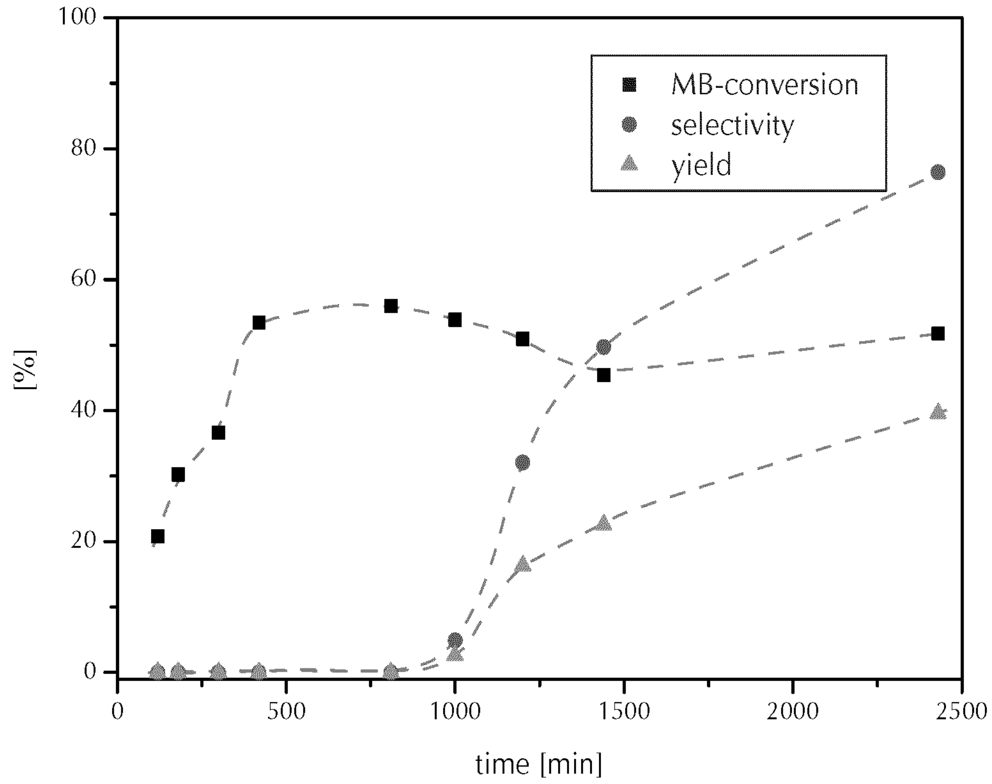

Fig. 4-4: Longterm experiment; MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB) vs. time. Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 9.4 g Deloxan ASP I/9 catalyst. Dashed lines are drawn as a guide for the eyes.

4.4 Parametric Sensitivity

The influence of the following parameters on the condensation reaction was investigated: pressure, temperature, total liquid flow rate, molar ratio and pre-treatment of the catalyst. Only one parameter was changed at the time while keeping otherwise standard conditions (see Chapter 2.1).

4.4.1 Temperature

The effect of temperature is illustrated in Figure 4-6 and Figure 4-7, respectively.

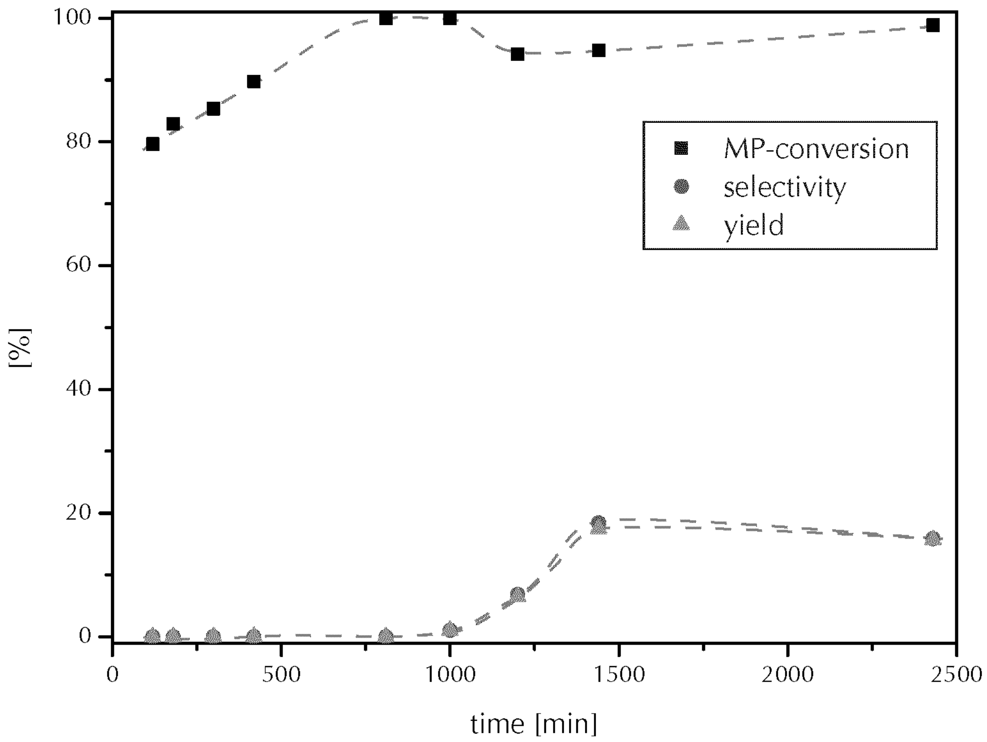

Fig. 4-5: Longterm experiment; MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP) vs. time. Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 9.4 g Deloxan ASP I/9 catalyst. Dashed lines are drawn as a guide for the eyes.

Behaviour related to MB

MB-conversion showed a step increase above ca. 110 °C which was accompanied by a dramatic drop in selectivity to the desired C8AK product (Figure 4-6). At about 110 °C moderate conversion combined with relatively high selectivity afforded reasonable yield of the desired product.

Behaviour related to MP

Performance characteristics related to MP (Figure 4-7) showed a similar behaviour as related to DLL. A complete loss of selectivity above a temperature of about 110 °C was observed, whereas conversion reached 100 %. This behaviour is attributed to undesired polymerization reactions and formation of other side products (MSO, DAA, MPD, IP) which became favoured at higher temperature. At low temperature mainly MBAdd (that did not rearrange to C8AK) and MPD were detected.

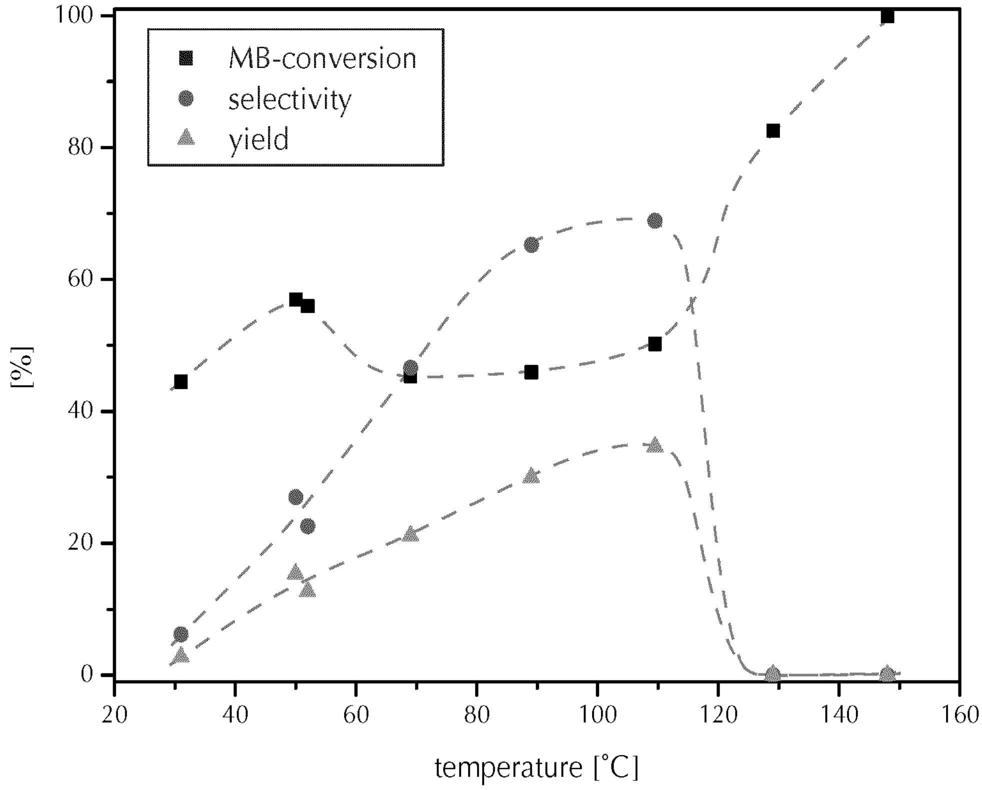

Fig. 4-6: Influence of temperature on MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB). Conditions: 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

4.4.2 Pressure

Figure 4-8 and Figure 4-9 show that a change in pressure from 11.5 bar to 100 bar had only minor influence on conversion, selectivity and thus yield of the desired product.

Behaviour related to MB

Conversion, selectivity and yield related to MB changed only little with increasing pressure.

Behaviour related to MP

MP-conversions slightly improved with increasing pressure, whereas selectivity and yield remained almost constant.

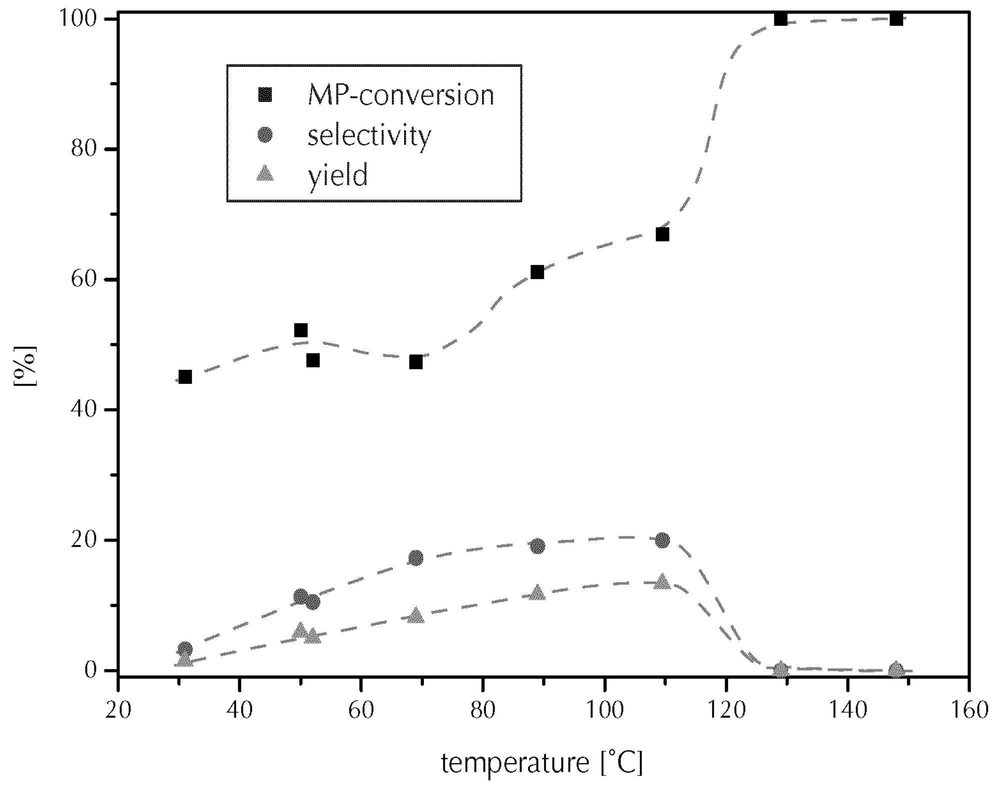

Fig. 4-7: Influence of temperature on MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP). Conditions: 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

Note that above 10 bar and 110 °C, MP (b.p. ca. 34 °C) and MB (b.p. ca. 102 °C) are both liquid, whereas below ca. 6 bar, MP changes to gas phase which influenced the reaction pathway by favouring gas phase reactions of MP at lower pressure.

4.4.3 Total Flow

Changing the total feed flow from 1.51 ml min^{-1} to 0.31 ml min^{-1} (corresponding to LHSV's of 12.1 to 2.5 h^{-1}) increased conversion of MB and MP (Figure 4-10 and Figure 4-11).

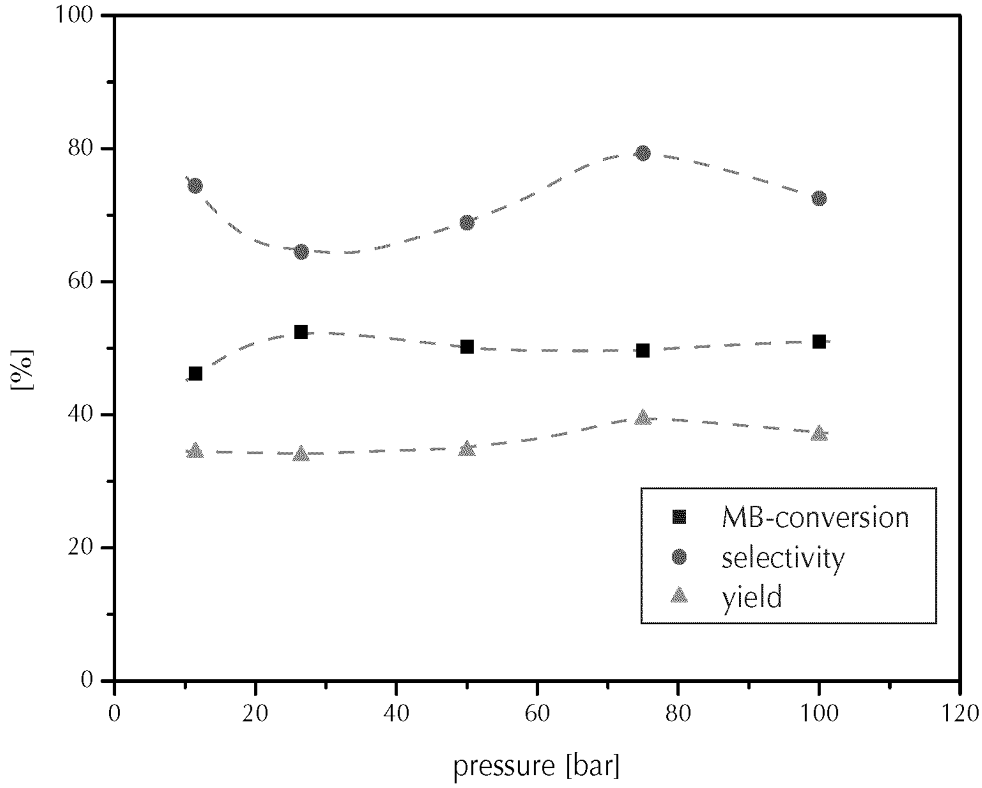

Fig. 4-8: Influence of pressure on MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB). Conditions: 110 °C, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

Behaviour related to MB

Longer residence times (lower flow rate) afforded higher MB-conversion and selectivity to C8AK related to reacted MB. As a consequence, yield related to MB increased with decreasing flow rate. In experiments with high flow rate the reaction pathway (reactions 1b, 2b and 3b) to the desired product was not completed. Intermediate MBAdd, which did not react further to the desired C8AK, was observed in the product stream.

Behaviour related to MP

Although lower flow rate led to higher conversion, undesired side reactions of MP (reactions 5, 6, 7, 10 and 11, Figure 4-3) became more prominent. However, this decrease in selectivity was not as strong as the increase of conversion, and consequently yield increased with lower flow rate.

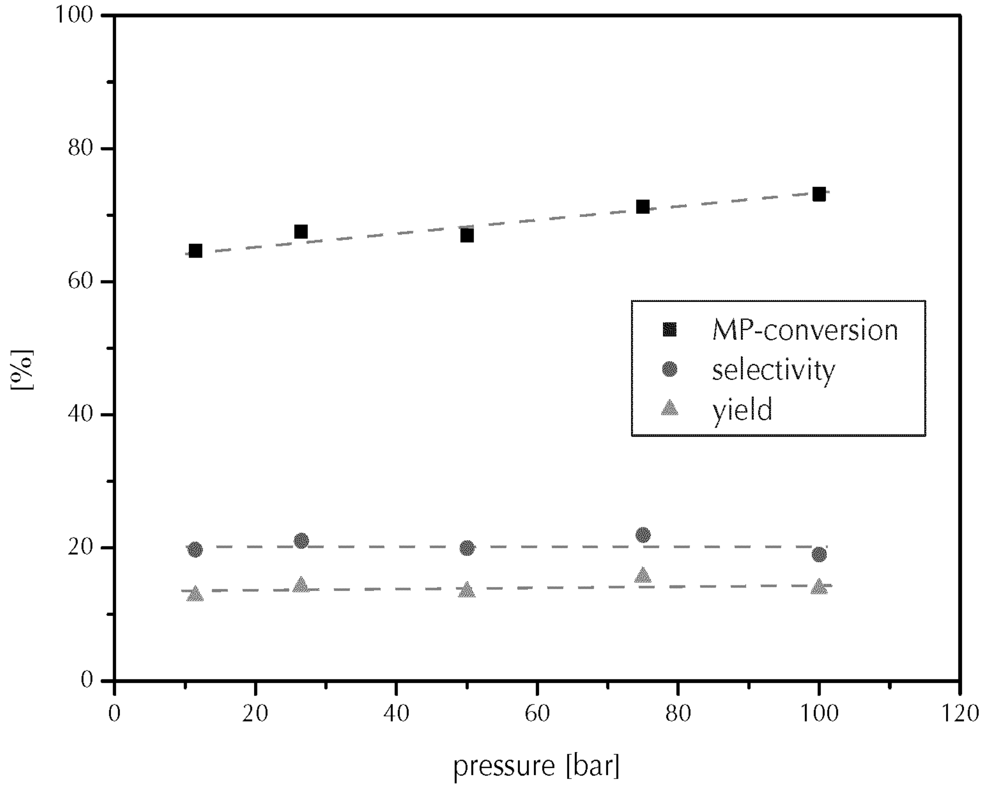

Fig. 4-9: Influence of pressure on MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP). Conditions: 110 °C, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

4.4.4 Molar Ratio

From a stoichiometrical point of view, a molar ratio (MP/MB) of 2 is expected to be optimal (Figure 4-1).

Behaviour related to MB

In reality, as shown in Figure 4-12, at a molar ratio of 6.2 a slightly higher MB-conversion was observed than at the theoretical optimum. This can be explained by a higher availability of MP-molecules to form the desired product together with MB. It can be expected that at even higher molar ratios MB-conversion and selectivity related to MB would even increase further, but on cost of a decrease of corresponding MP values.

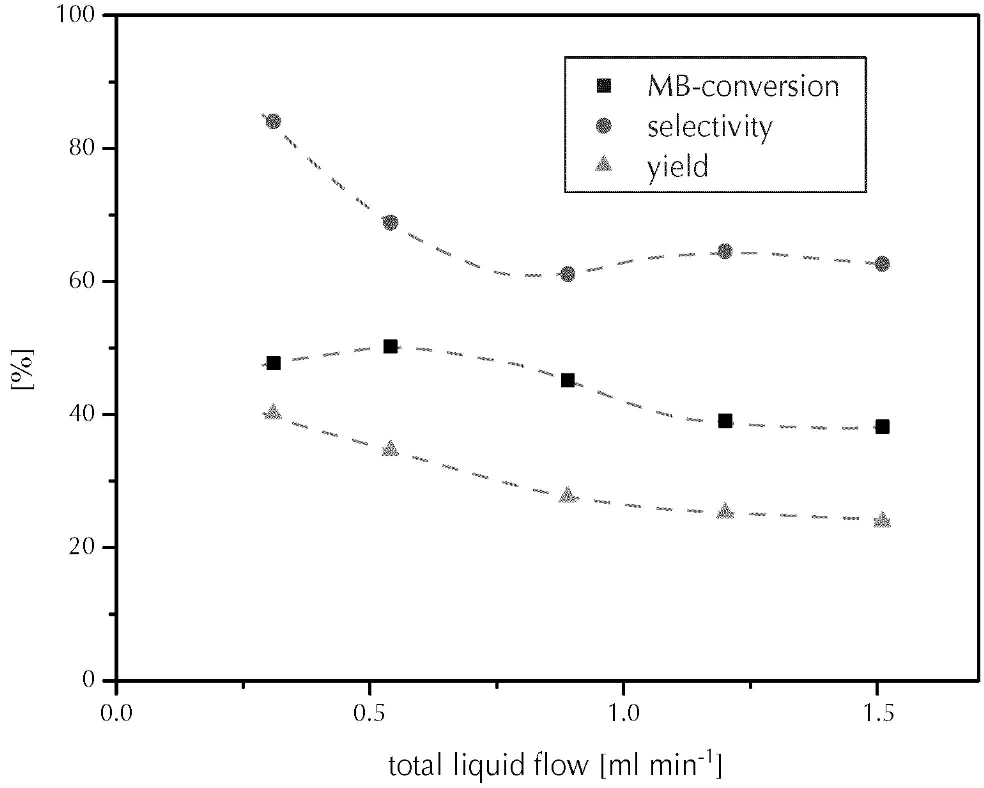

Fig. 4-10: Influence of flow rate on MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB). Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

Behaviour related to MP

Related to MP, best results were observed close to the stoichiometrical ratio (c.f. Figure 4-13). Conversion, selectivity and yield showed highest values at a MP/MB ratio of about 1.5.

At the highest yield of C8AK related to MB (MP/MB ratio of 6.2), side reactions of MP were more favoured (reactions 5, 6, 7 and 10), which led to a decrease in selectivity to the desired C8AK related to MP.

4.4.5 Pretreatment

Finally, the influence of catalyst pretreatment (after the 24 h conditioning of larger amounts of catalyst; see also Chapter 2.2.2) was investigated (Figure 4-14 and Figure 4-15). Before pumping reactants into the reactor sys-

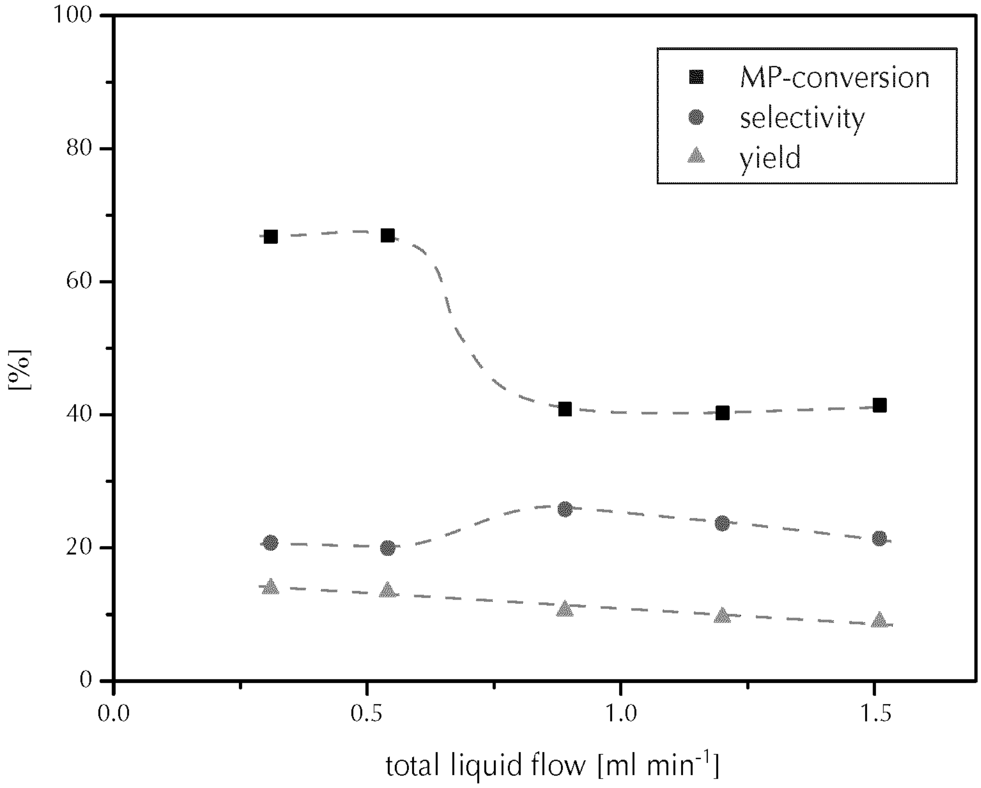

Fig. 4-11: Influence of flow rate on MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP). Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

tem, the catalyst was flushed for 30 min at reaction conditions with MP or MB alone, resp. with MeOH (3 ml min^{-1}).

Behaviour related to MB

Treatment with MP led to a lower MB-conversion and selectivity decreased. Overall, yield to C8AK related to MB decreased by 11 %.

After treatment with MB, almost the same catalytic behaviour was observed as after MP-pretreatment. Here also, conversion, selectivity and yield related to MB were lower than with untreated (preconditioned) catalyst.

Also pretreatment with MeOH showed worse results than the one without pretreatment. Values related to MB were lower than corresponding values obtained with untreated catalyst, but still higher than those after pretreatment with MP or MB.

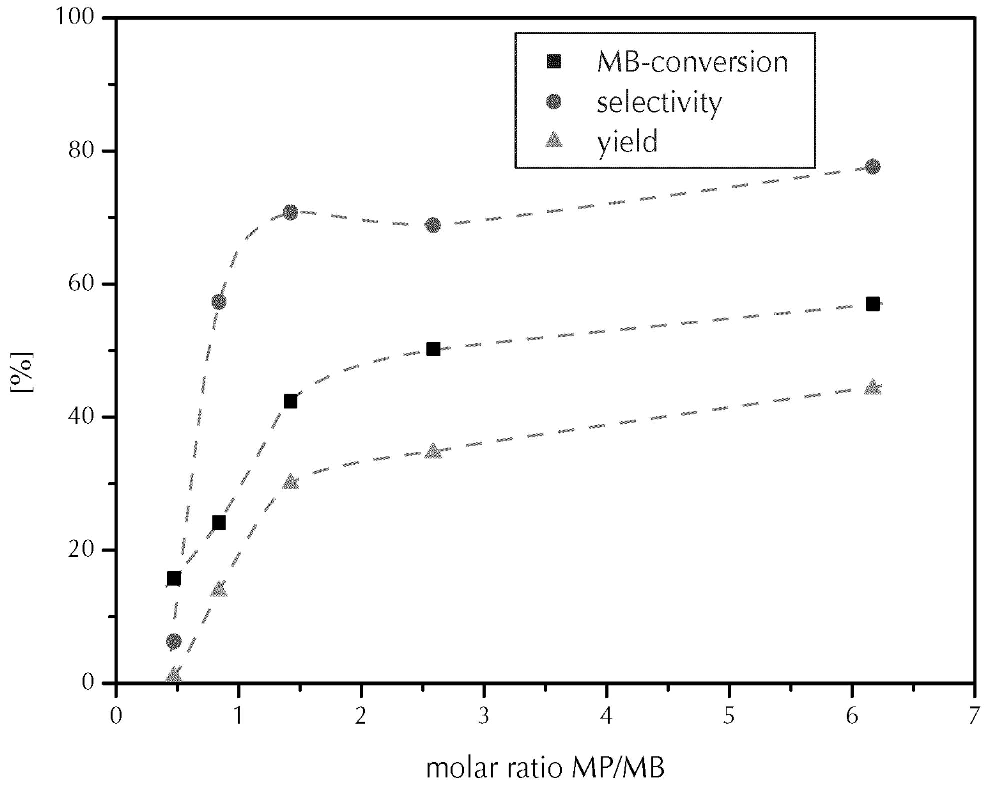

Fig. 4-12: Influence of molar ratio (MP/MB) on MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB). Conditions: 110 °C, 50 bar, total flow rate: 0.54 ml min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

Behaviour related to MP

Catalyst pretreatment with MP led to a decrease in conversion but selectivity related to MP increased slightly compared to untreated catalyst. Yield related to MP remained at about the same level.

Concerning catalyst pretreatment with MB, the same behaviour could be observed.

Finally pretreatment with MeOH resulted in a higher conversion and a similar selectivity as with untreated catalyst. Yield related to MP slightly increased compared to standard experiment (no pretreatment, only 24 h conditioning).

This result is not surprising, considering the possibility of a catalyst surface cleaning (decontamination) with MeOH. In the case of pretreatments with MP and MB this decontamination seems not to be effective. Even worse, new

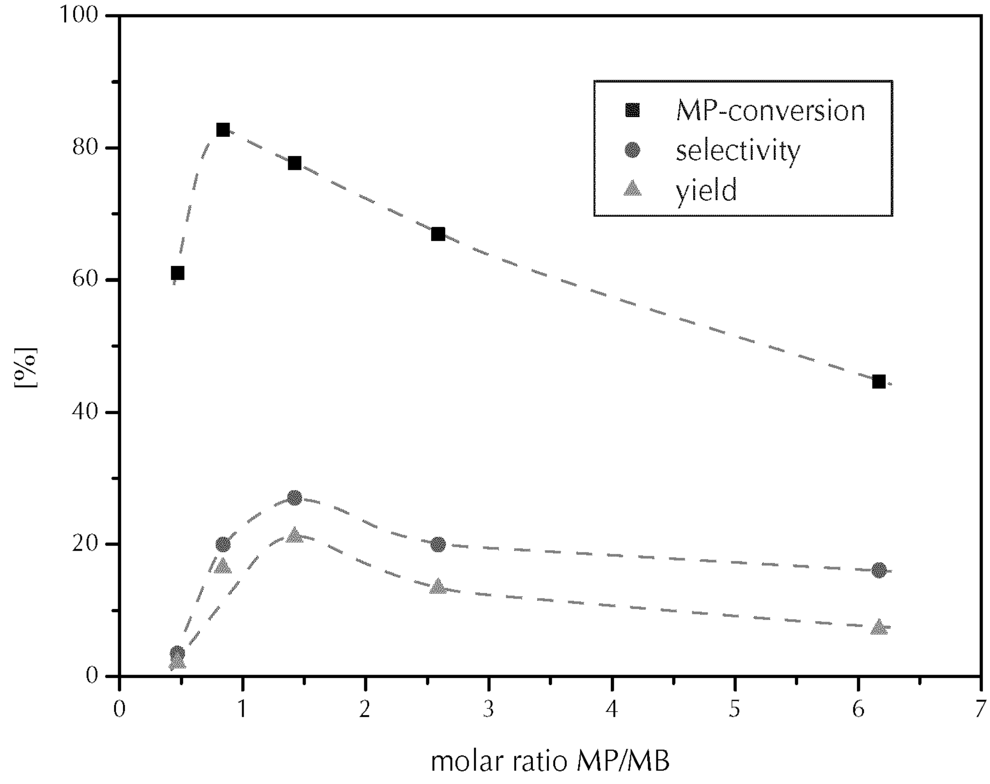

Fig. 4-13: Influence of molar ratio (MP/MB) on MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP). Conditions: 110 °C, 50 bar, total flow rate: 0.54 ml min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions). Dashed lines are drawn as a guide for the eyes.

contaminations occurred due to side reactions. Although effective for a short time, pretreatment with MeOH did not result in improved catalytic behaviour after 4 h.

4.5 Conclusions

The heterogeneously catalyzed ketonization reaction of 2-methyl-3-butyn-2-ol and 2-methoxypropene was carried out in a continuous flow reactor system. Deloxan ASP I/9 (a solid alkyl sulfonic acid polysiloxane catalyst from Degussa) was used as catalyst. A longterm experiment served to determine time on stream behaviour of this catalyst. A time on stream of about 24 h was neces-

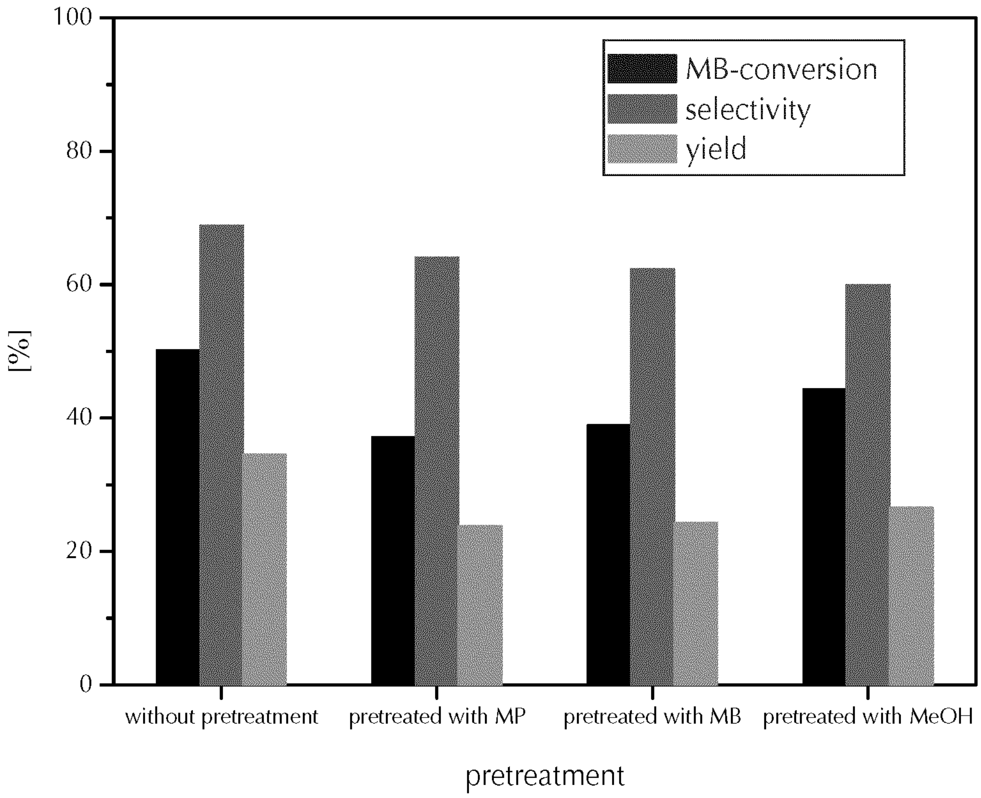

Fig. 4-14: Influence of catalyst pretreatment on MB-conversion, selectivity to C8AK (related to MB) and yield of C8AK (related to MB). Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions), pretreatment with indicated substance for 30 min (3 ml min^{-1}) at reaction conditions.

sary to activate and condition the catalyst to selectively produce the desired product.

Analyzed product streams almost exclusively consisted of products that were expected, compared to studies described in literature: main products were the desired ketone C8AK and co-product DMP. MB-MP-addition product (MBAdd) and MP-dimer (MPD) were the main intermediate- resp. side-products, whereas various other side-products, were only found in small amounts (MeOH, acetone, DAA, MSO, IP etc.).

Parametric sensitivity studies showed the influences of temperature, pressure, total liquid flow, molar ratio MP/MB and catalyst pretreatment with different pretreatment agents at reaction conditions.

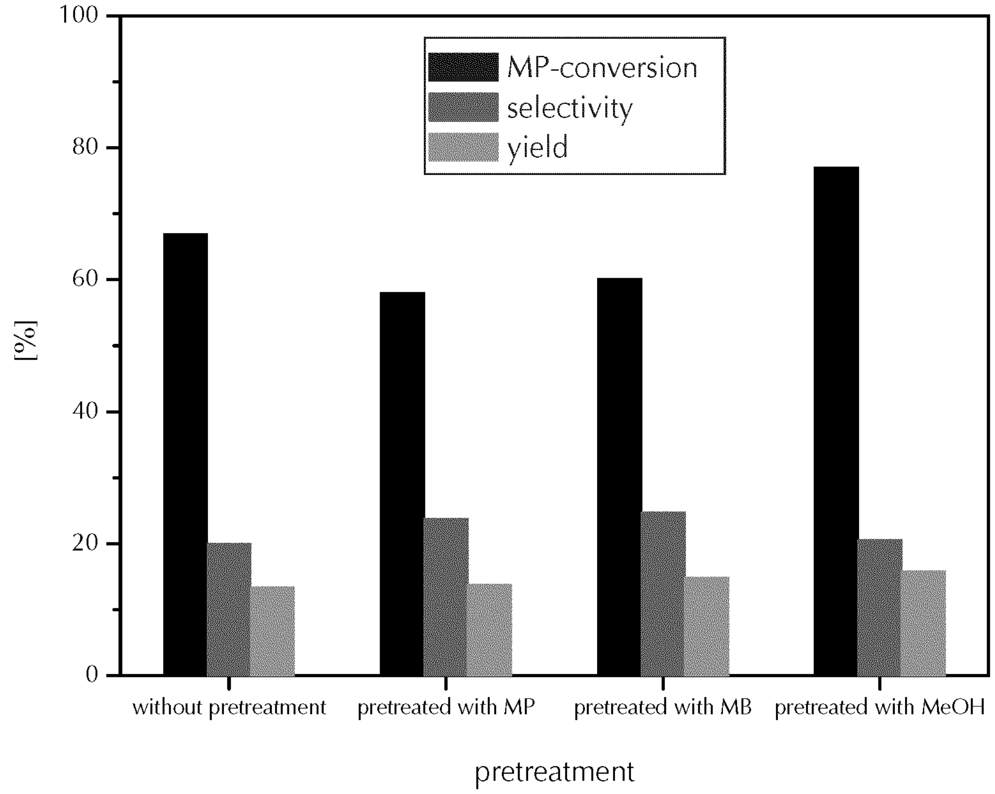

Fig. 4-15: Influence of catalyst pretreatment on MP-conversion, selectivity to C8AK (related to MP) and yield of C8AK (related to MP). Conditions: 110 °C, 50 bar, molar ratio MP/MB=3, 0.4 ml MP min^{-1}, 0.14 ml MB min^{-1}, 4 g Deloxan ASP I/9 catalyst (conditioned for 24 h at reaction-conditions), pretreatment with indicated substance for 30 min (3 ml min^{-1}) at reaction conditions.

The influence of temperature was striking. C8AK-yield increases steadily with temperature up to about 115 °C, but then drops, due to a complete loss of selectivity to C8AK.

Pressure showed only a weak influence on catalytic results: C8AK-yield remained at an almost constant level over a large pressure range (11.5 bar-100 bar).

Changes in liquid flow rate resulted in the following behaviour: increasing flow rates (increasing LHSV's) led to decreasing yield.

Variation of the molar ratio MP/MB showed a C8AK-yield optimum at a ratio of about 1.5 related to fed MP. Considering results related to MB, an increase of the molar ratio MP/MB led to a continuous increase of yield in the observed range.

Finally, a pretreatment of the catalyst (which was previously conditioned for 24 h at reaction conditions) with MP, MB resp. MeOH showed that none of the three pretreatment agents improved catalytic performance compared to untreated catalyst. Only C8AK-yield related to MP of the MeOH pretreated catalyst was higher than the corresponding value from the experiment with untreated catalyst.

Yields of about 40 % of the desired product (related to MB) could be achieved with this solid acid catalyst. However, compared to results described in literature, the heterogeneous catalysts investigated can not compete with the best homogeneous catalysts. Note that the homogeneously catalyzed reaction results in literature were achieved in batch reactor systems, with inherent separation problems.

4.6 Comparison of C13AK- and C8AK-Synthesis

The results gathered for C13AK- and C8AK-syntheses allow a comparison of the catalytic behaviour observed for these reactions. DLL- and MB-ketonization studies were both performed under similar conditions. Reactant-conversions and ketone-selectivities related to the unsaturated alcohols (DLL resp. MB) and to the unsaturated ether (in both cases MP) were compared at different reaction conditions.

In general, reactions with MB resulted in higher conversions of both reactants (alcohol and ether). Also product-selectivities (C13AK, C8AK) were usually higher in MB- than in DLL-ketonization. These observations may be traced to the fact that MB-molecules are much smaller and possess better accessibility to the catalyst surface than the relatively large DLL-molecules. The small MB-molecules more easily reach active catalyst sites in pores and thus a larger surface area is accessible for reactions between the alcohol and the ether. It is likely that during DLL-ketonization some active sites are only accessible for MP-molecules, which favours undesired side reactions.

4.6.1 Time on Stream Behaviour

For both ketonization reactions longterm experiments were carried out to determine time on stream behaviour.

Whereas DLL- and MB-conversions reached an almost constant level after a relatively fast increase after reaction start, MP-conversions on the other hand behaved differently in the two reactions. In DLL-ketonization, MP-conversion started at almost 100 % and slowly decreased with time, whereas in MB-ketonization, MP-conversion first increased and then remained at nearly 100 %.

A different behaviour could also be observed concerning selectivity to the desired product (C13AK resp. C8AK). Related to the unsaturated alcohols, in the case of DLL, a fast increase and reaching of a constant level could be observed, whereas in the case of MB a longer catalyst conditioning time was necessary to even produce the desired ketone. In MB-ketonization, even after 40 h on stream, an increase in selectivity could be observed (no reaching of a constant level). Related to the unsaturated ether (in both cases MP), selectivity behaved as for the alcohols (fast increase and reaching of a constant level for DLL-ketonization and longer induction period necessary for MB-ketonization).

The reason for this behaviour is not understood yet, but has probably to be sought in the complex dynamical changes of the catalyst surface as a result of the various products interacting with the acidic surface sites.

4.6.2 Temperature

In DLL-ketonization DLL- and MP-conversion showed only weak dependence on temperature, whereas in MB-ketonization the effect of temperature was more prominent. Selectivities to the desired product (related to DLL resp. MB and MP) showed marked differences. Selectivity in MB-ketonization dropped completely above ca. 110 °C (related to both MB and MP). At higher temperature, only undesired reactions were observed.

4.6.3 Pressure

In both reactions, conversion and selectivity were only weakly dependent on pressure changes in the investigated pressure range. Only MP-conversion in C8AK-synthesis slowly increased with higher pressure, all the other performance characteristics remained at approximately constant levels. Thus we can conclude that pressure only weakly influenced the catalytic behaviour of both reactions.

4.6.4 Total Flow

Changes of total flow rate had also a similar effect in both reactions. Related to the unsaturated alcohols (DLL resp. MB) the following behaviour was observed: In both reactions conversion decreased with decreasing residence time. Selectivity, on the other hand, increased with increasing flow for C13AK-synthesis, whereas the opposite was the case for C8AK-synthesis.

Concerning sensitivity to total liquid flow rate, and thus change of residence time, MP-conversion and selectivity related to MP behaved similarly: Conversion continuously decreased with increasing flow rate and selectivity showed a local optimum (at a flow rate of about 0.6 ml min^{-1} for C13AK- resp. 0.9 ml min^{-1} for C8AK-synthesis) in both reactions.

4.6.5 Molar Ratio

Increasing molar ratio (of ether to alcohol) led in both reactions to an increase in alcohol-conversion. Selectivity related to DLL resp. MB on the other hand behaved differently. An increase in molar ratio (MP/DLL) in DLL-ketonization resulted in a selectivity maximum at a molar ratio of about 0.8 with continuously decreasing values above that ratio. In MB-ketonization, however, strong increase in selectivity between a molar ratio (MP/MB) of 0.5 to 1.5 and a weaker increase above a ratio of 1.5 could be observed.

At low MP/alcohol-ratios, selectivity related to the alcohol MB was lower than the one related to DLL. This observation could be explained by the larger accessible catalyst surface area for smaller MB-molecules, which may enhance undesired side reactions.

Values related to MP showed similar behaviour for both reactions. Conversions and selectivities decreased with increasing molar ratio (ether/alcohol) with the exception of an increase of both conversion and selectivity from a molar ratio of 0.5 to 1.5 in MB-ketonization.

4.6.6 Pretreatment

Different catalyst pretreatment steps led to the following results related to unsaturated alcohols (DLL resp. MB) for the ketonization reactions: only pretreatment with MeOH led to an increase in DLL-conversion and also higher C13AK-selectivity compared to untreated catalyst, whereas for MB-ketonization, untreated catalyst showed the best performance (conversion and selectivity).

Related to the unsaturated ether MP, a slightly different behaviour could be observed. In both ketonization reactions, catalyst pretreated with MeOH showed better conversion and selectivity than untreated catalyst.

Pretreatment of the catalyst for C8AK-synthesis had no positive influence on catalytic results as was the case with MeOH as catalyst pretreatment agent before use in C13AK-synthesis.

Chapter 5

Ketonization in Batch Reactor using "supercritical" CO_2 as Solvent

5.1 Introduction

Due to technical problems in the continuous flow reactor system (cf. Chapter 2.2.3), investigations with "supercritical" fluid as solvent for the ketonization reactions had to be carried out in a batch reactor system. Even more, batch reactor experiments with different solvents are easier to compare than the same experiments in a continuous flow reactor. The question whether "supercritical" CO_2 as solvent is preferable to a conventional solvent (toluene) or to solventless processing had to be answered. In theory, "supercritical" CO_2 has the power to clean catalyst surfaces from deactivating contaminants such as carbonaceous residues and presents optimum transport properties for reactants, which makes it an optimal solvent for several known processes (cf. Chapter 1.4). In this work, the term "supercritical" is used as defined in Chapter 1.4. Conversion, selectivity and yield were calculated according to the definitions given in Chapter 2.3.

To compare results of this work with values from literature [2, 6], data from previous homogeneous catalytic studies are presented in Table 5-1.

5.2 2-Methyl-3-butyn-2-ol-Ketonization

In batch reactor studies with MB, the same reaction products could be observed as in the product streams from continuous flow experiments (c.f. Chapter 4.2).

Tabelle 5-1: Yields of ketonization reactions carried out in batch reactors (2-methoxypropene was used as unsaturated ether) [2, 6].

cited literature	alcohol	catalyst	product	reaction time [h]	$Y_{prod., alc.}$ [%]
Patent EP 1 092 700 A1	MB	methane sulfonic acid	C8AK	6.5	89
	MB	pyridinium-toluene-4-sulfonate	C8AK	6.5	91
	DLL	methane sulfonic acid	PI	6	92
	DLL	pyridinium-toluene-4-sulfonate	PI	6	92
Saucy-Marbet Helv. Chim. Acta 1967	MB	p-toluene sulfonic acid	C8AK	15-24	95[a]
	DLL	p-toluene sulfonic acid	C13AK	17	95[b]

[a] calculated yield from described experiment: 94.1 %.

[b] calculated yield from described experiment: 83.3 %.

Catalytic results of batch reaction experiments of MB-ketonization in the conventional solvent toluene, as presented in Table 5-2, did not substantially change by increasing pressure from 10 to 91 bar (runs 1 and 2) (only selectivity related to MB rose from 90 to 99 % which led to a small increase in yield of about 4 %).

Using CO_2 as solvent for the same reaction, performance values showed bigger differences between experiments at different pressures (runs 4 and 5). Compared to an experiment at 10 bar, at 97 bar conversion was lower but at higher selectivity (formation of DMP less favoured than at low pressure). This, overall, led to higher yield at higher pressure.

Comparing the results with CO_2 as solvent at high pressures (runs 3 and 5; 85 bar after 2 h and 97 bar after 4 h), conversion increased with reaction time,

Table 5-2: 2-methyl-3-butyn-2-ol-ketonization in a batch reactor system. Conditions: 110 °C, molar ratio MP/MB=3, 14.9 ml MP, 5.1 ml MB, 75 ml toluene resp. CO_2, 500 rpm, 0.5 g Deloxan ASP I/9 catalyst (conditioned for 24 h at "standard conditions", see Chapter 2.2.2).

Run	Solvent	Pressure [bar]	Reaction time [min]	X_{MP} [%]	X_{MB}[%]	$S_{C8AK, MB}$ [%]	$S_{C8AK, MP}$ [%]	$Y_{C8AK, MB}$ [%]	$Y_{C8AK, MP}$ [%]
1	Toluene	10	240	83.5	48.3	90.4	19.1	43.7	15.9
2	Toluene	91	240	82.0	47.6	99.5	18.0	47.4	14.8
3	CO_2	85	120	43.5	25.3	95.1	17.5	24.1	7.6
4	CO_2	10	240	83.9	33.4	63.6	8.2	21.3	6.9
5	CO_2	97	240	73.7	31.8	82.1	11.5	26.1	8.5
6	none	49	120	57.3	27.1	76.5	11.7	20.7	6.7
7	none	88	120	55.9	25.1	80.2	11.7	20.1	6.5

whereas selectivity decreased (DMP-formation becomes more favoured with time).

As for reactions in toluene, a pressure increase from 49 to 88 bar did not affect catalytic results of the solventless reaction (runs 6 and 7; nitrogen was used as inert gas to build up pressure in the system).

Comparing results with the two different solvents (at both pressure levels; runs 1 and 4 resp. runs 2 and 5), experiments in toluene showed better performance (X, S and Y). The good selectivity obtained with toluene could not be improved by applying "scCO_2". In fact, only about half of the yield achieved with toluene could be accomplished. Possible removal of catalyst deactivating products or better mass transfer with "supercritical" CO_2 were not effective.

A comparison of results between solventless processing and experiments with CO_2 (runs 3 and 7; after 2 h at 85 resp. 88 bar) showed that the use of CO_2 brought an advantage of about 4 % in yield of desired product related to MB. Although conversion was lower in CO_2, selectivity was much higher and thus lead to increase of yield. This behaviour is attributed to improved mixing and energy dissipation in the presence of "$scCO_2$". In the solventless reaction less efficient energy dissipation may cause temperature gradients in the reaction mixture which may enhance the formation of undesired side products.

Note that reaction times in this work (heterogeneous catalyst) were shorter than those described in other studies (homogeneous catalysts) and reaction conditions were not optimized. Selectivity (related to MB) was high, whereas conversion was relatively low due to shorter reaction times.

5.3 Dehydrolinalool-Ketonization

Concerning observed reaction products in batch DLL-ketonization reactions, no differences could be noticed compared to continuous flow experiments (c.f. Chapter 3.3). A comparison of catalytic results of DLL-ketonization reactions with conventional solvent (toluene), with "$scCO_2$" as solvent and without solvent is presented in Table 5-3.

As for experiments with MB, catalytic results for DLL-ketonization with toluene as solvent were not considerably influenced by pressure changes (runs 8 and 9). Only selectivity related to DLL and thus yield were lower at high pressure. This weak pressure sensitivity was not surprising, since toluene is not known as solvent whose properties change strongly in the observed pressure range.

In "$scCO_2$", conversion (related to DLL) decreased and selectivity, which was already very high at low pressure, remained the same with increasing pressure (runs 11 and 12). Values related to MP behaved differently: conversion remained almost constant at 51.5 % and selectivity only slightly decreased from 19 to 17 %. Compared to experiments with MB, the influence of pressure was not strong when using "$scCO_2$".

Also in experiments with DLL, with "$scCO_2$" as solvent, conversions increased with reaction time (runs 10 and 12; 88 bar after 2 h and 97 bar after 4 h), as expected. Here also selectivity related to DLL increased, which was, however, compensated by a decrease of selectivity related to MP. Intermediate DLLAdd (DLL-MP-addition product) formed after 2 h reacted further to the

Table 5-3: Dehydrolinalool-ketonization in a batch reactor system. Conditions: 110 °C, molar ratio MP/DLL=3, 12.4 ml MP, 7.6 ml DLL, 75 ml toluene resp. CO_2, 500 rpm, 0.5 g Deloxan ASP I/9 catalyst (conditioned for 40 h at "standard conditions", see Chapter 2.2.2).

Run	Solvent	Pressure [bar]	Reaction time [min]	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, DLL}$ [%]	$S_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$ [%]
8	Toluene	10	240	18.2	11.3	64.7	14.6	7.3	2.6
9	Toluene	92	240	19.3	11.7	55.8	12.3	6.6	2.4
10	CO_2	88	120	23.2	17.0	81.1	17.9	13.8	4.2
11	CO_2	11	240	51.6	26.6	99.2	19.0	26.4	9.8
12	CO_2	97	240	51.4	23.5	99.8	16.8	23.5	8.6
13	none	43	120	32.5	21.5	67.5	16.3	14.5	5.3
14	none	83	120	30.1	20.0	90.4	18.2	18.1	5.5

desired product C13AK after 4 h, which explains the increase in selectivity related to DLL.

Performing experiments without solvent, an increase in selectivity by raising pressure from 43 to 83 bar could be observed (runs 13 and 14; N_2 was used to reach desired pressure in reactor), which led to higher yields of desired product at higher pressure. At lower pressure, on the other hand, higher amounts of DLLAdd could be observed that could react further to the desired product C13AK (in a thermal reaction). The increase in selectivity with increasing pressure is not so beneficial when considering a potential consecutive reaction of DLLAdd from the low pressure experiment.

We can state that in DLL-ketonization, the use of "scCO_2" instead of toluene as solvent brought significant improvement of catalyst performance (runs 11 and 8 resp. runs 12 and 9). Relatively large DLL-molecules and small MP-molecules had to be mixed for reacting to the desired product. "scCO_2" instead of toluene as solvent apparently improved mixing of these two unequal reactants. Conversions more than doubled and also selectivities increased markedly, which lead to yields more than three times as high as with the conventional solvent.

However, application of "$scCO_2$" as solvent did not surpass results reached in reactions without solvent. A comparison of catalytic results obtained without solvent and experiments with "$scCO_2$" (runs 14 and 10) shows that for DLL-ketonization, the use of CO_2 as solvent does not lead to an improvement, as also observed for MB-ketonization. An obvious improvement of mixing conditions or removal of undesired carbonaceous deposits on the catalyst by using "supercritical" CO_2 could not be confirmed.

In DLL-ketonization, conversion in toluene was much lower compared to that achieved in the solventless reaction (runs 9 and 14). Interestingly, selectivity and yield were lower than in the solventless reaction. Thus, in this case, introduction of a solvent did not bring significant advantages.

Compared to published C13AK-yields achieved with homogeneous catalysts, none of the heterogeneously catalyzed experiments carried out in this work afforded comparable results (95 % vs. 26.5 %). Considering the shorter reaction times in this work compared to those described in literature, possibly some potential still lies in the application of these solid acid catalysts.

5.4 Conclusions

Ketonization reactions of 2-methyl-3-butyn-2-ol (MB) resp. dehydrolinalool (DLL) with 2-methoxypropene (MP) were carried out in an autoclave system to investigate catalytic reaction behaviour with conventional solvent (toluene), with "supercritical" carbon dioxide ("$scCO_2$") as solvent resp. without a solvent at pressures of 10 and 90 bar. Experiments with "$scCO_2$" as solvent for the MB-ketonization reaction afforded yields of desired product that were only half as high as yields achieved with conventional solvent (toluene). In contrast, the use of "$scCO_2$" as solvent for DLL-ketonization tripled yields to the desired product compared to the conventional solvent. However, compared to results without solvent no real improvement of the reaction performance could be observed in the case of “$scCO_2$” as solvent.

Chapter 6

In situ ATR-IR Spectroscopy

6.1 Introduction

The previous catalytic studies showed that selectivities related to MP were always considerably lower than corresponding selectivities related to the alcohol (DLL or MB, respectively). This prompted us to investigate the interaction of MP with the acidic catalyst in more detail. It was hoped that this would help for better understanding the Saucy-Marbet-type condensation reactions with acidic solid catalysts. In these reactions, the first acid catalyzed reaction step consists of a condensation of a vinyl ether with an unsaturated alcohol. A subsequent thermal step leads to an unsaturated ketone [1]. Vinyl ethers can furthermore easily be hydrolyzed in the presence of acids. This reaction has been studied thoroughly in homogeneous phase. From these studies it emerged that the rate-limiting step is proton-transfer [146]. Protonation takes place at the β-carbon of the vinyl ether and not at the oxygen, giving rise to a stable carbocation [147].

In our group attenuated total reflection (ATR) infrared spectroscopy [148] has been used in previous studies to explore solid-liquid interfaces consisting of thin metal films [142, 149], supported metals [143, 150] and oxide catalysts [151]. Here the technique is applied to investigate the complex transformation of a simple vinyl ether, 2-methoxypropene, with solid acid catalysts based on silica modified with sulfonic and sulfuric acid.

6.2 Results

6.2.1 Characterization of the Sulfonic Acid Groups of Deloxan

The surface of Deloxan ASP I/9, which contains 3-propane sulfonic acid groups (Figure 6-1), showed signals at 3737, 2979, 2952, 2898, 1725, 1636, 1459, 1415 and 1355 cm^{-1} (DRIFT). Signals associated with the SiO_2 matrix were found at 1094, 948 and 802 cm^{-1}.

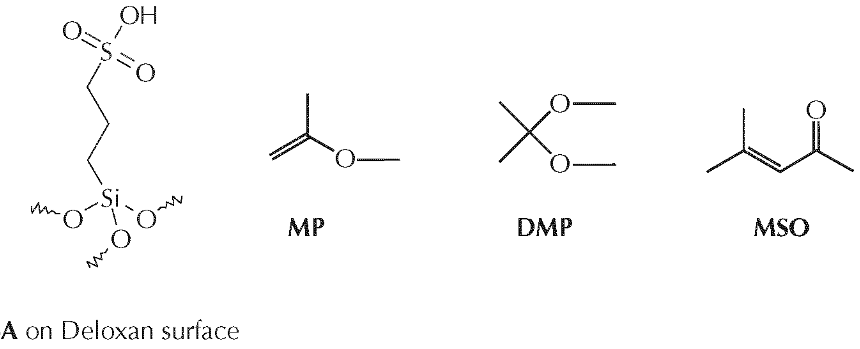

Fig. 6-1: Structure of the surface 3-propane sulfonic acid groups of Deloxan as well as of 2-methoxypropene (MP), 2,2-dimethoxypropane (DMP) and mesityloxide (MSO).

1-Propane sulfonic acid (PSA) in hexane solvent showed absorptions at 3649, 3438, 2967 (2975 cm^{-1} for neat PSA), 2939 (2941), 2880 (2885), 1461, 1370, 1340, 1296, 1170, 1095, 1071 and 1012 cm^{-1}. The signals at around 2900 cm^{-1} can be assigned in both cases to the C-H stretchings of the methylene and methyl groups of PSA. The signal at 3737 cm^{-1} found in Deloxan reveals the presence of free silanol groups. The signal at ca. 1460 cm^{-1} is likely due to the deformation mode of CH_2 groups.

Sulfonic acid groups were assigned by following the behaviour of the typical signals of PSA upon addition of a base. Titration of PSA with pyridine in hexane solvent indicated that signals at 1370 and 1170 cm^{-1} have to be assigned to the characteristic stretching vibrations of S=O groups. Consistently, these signals were attenuated at increasing pyridine concentration and completely disappeared at equivalence, whereas new bands grew in at 1233 and 1140 cm^{-1}. Sulfonic acids absorb at 1350-1342 cm^{-1} (ν_{AS}) and 1165-1150 cm^{-1} (ν_S), whereas sulfonates at 1372-1335 cm^{-1} and 1195-1168 cm^{-1} [152]. Hence, the signal of Deloxan at 1355 cm^{-1} is likely due to SO_3^- groups.

The broad signal around 1725 cm^{-1} observed in the DRIFT spectrum in air can be assigned to the deformation vibration of hydronium ions. In a dehydration study of Nafion membranes (perfluorinated polymeric sulfonic acid, trademark of E.I. du Pont de Nemours Co.) a broad signal has been observed at around 1720 cm^{-1} and assigned to a deformation vibration of hydronium ions [153].

6.2.2 Pyridine Adsorption on SiO_2 and Deloxan

Pyridine is an excellent probe for investigating the acidity of solid materials since its adsorption on Lewis and Brønsted acid sites affords distinctly different sets of signals in the two cases. Figure 6-2 shows the ATR spectra of pyridine

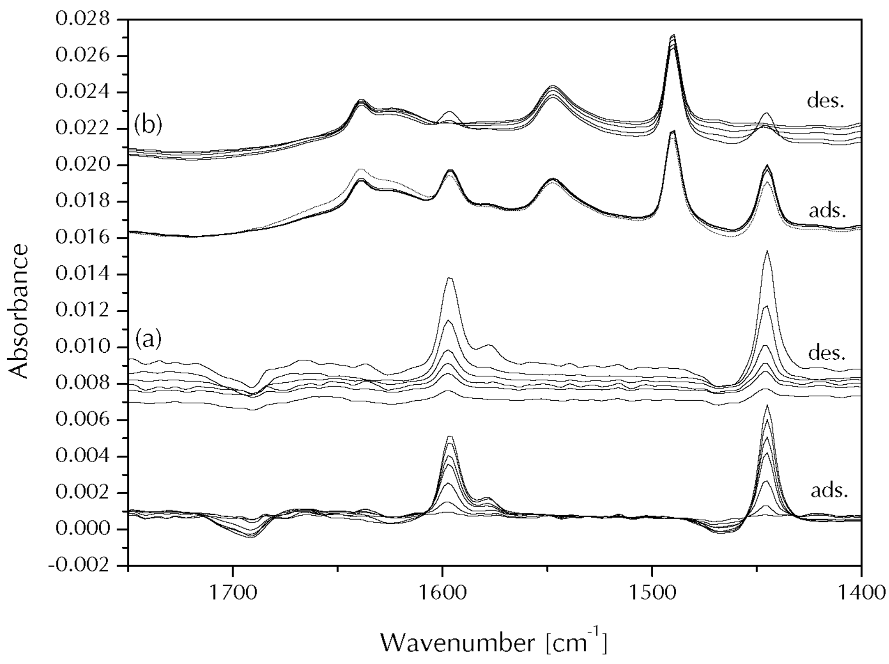

Fig. 6-2: ATR spectra of pyridine adsorption on (a) SiO_2 and (b) Deloxan from a 10^{-2} M solution in hexane as function of time. Adsorption and desorption steps are shown for both materials. During the desorption step neat solvent was flown over the sample.

contacted with (a) SiO_2 and (b) Deloxan from a 10^{-2} M solution in hexane. The SiO_2 surface displays the typical signals due to pyridine hydrogen-bonded to silanol groups, which is labelled HPy. These signals are found at 1595, 1578 and 1445 cm^{-1} and are almost completely attenuated due to desorption when flowing neat hexane solvent.

In contrast to SiO_2, Deloxan exhibits three additional bands at 1638, 1550 and 1490 cm^{-1}, which are assigned to pyridinium ions bound to Brønsted acid sites (BPy) [154]. These sites are associated with the sulfonic acid groups present on the Deloxan surface. The very broad negative band around 1725 cm^{-1} and the broad positive band at 1620 cm^{-1} arising upon pyridine adsorption indicate the transformation of hydronium ions to water. Hence pyridine is protonated by the hydronium ion. On desorption, the signals due to HPy are almost completely attenuated, whereas those corresponding to BPy are only slightly affected showing that pyridine strongly binds to the Brønsted sites of the Deloxan surface. Table 6-1 summarizes the assignment of the observed signals for pyridine on SiO_2 and Deloxan.

Table 6-1: Observed IR bands and assignment of ring-breathing vibrations for neat pyridine and adsorbed on SiO_2, Deloxan and sulfated TiO_2-modified amorphous SiO_2.

Neat	SiO_2	Deloxan	TiO_2-Mod. SiO_2	Mode	Assignment [155]
		1639	1638	*8a*	ν(CCN) BPy
1597	1597	1596	1596		ν(CCN) HPy
1580	1578	1578	1578	*8a*	ν(CCN) HPy
		1547	1544	*19b*	ν(CCN)+δ(CCN) BPy
		1489	1488	*19a*	ν(CCN)+δ(CCN) BPy
1481				*19a*	ν(CCN)+δ(CCN)
1439	1445	1444	1445	*19b*	ν(CCN)+δ(CCN) HPy

The relative concentration of Lewis and Brønsted acid sites, on which pyridine is adsorbed, can be estimated from the infrared spectra at saturation. The information needed is the absorption coefficient for the corresponding vibrational modes at 1445 (19b mode of pyridine) and 1550 cm^{-1} (19b mode of pyridinium ion). The relative concentration of Brønsted and Lewis sites C_B/C_L is $C_B/C_L = (A_{1550}/A_{1445})*(\varepsilon_{1445}/\varepsilon_{1550})$.

Here A_{1550} and A_{1445} are the integrated absorbances of the 19b modes at 1550 and 1445 cm^{-1}, associated with Brønsted and Lewis sites, and ε_{1550} and ε_{1445} are the absorption coefficients for the corresponding bands at 1550 and 1445 cm^{-1}. Values of 1.24 and 1.56 cm μmol^{-1} have been reported for ε_{1550} and ε_{1445}, respectively [156]. Using these values a relative concentration C_B/C_L of 1.3 can be estimated form the spectra. It should however be noted that for sulfated silica-zirconia mixed oxides the absorption coefficient ε_{1550} of the pyridinium ion was found to decrease significantly at high sulfate density [156].

6.2.3 Interaction of 2-Methoxypropene with SiO_2 and Deloxan

The ATR spectra of MP (10^{-3} M) on SiO_2 are depicted in Figure 6-3. A sharp signal develops at 1692 cm^{-1} with a shoulder at ca. 1700 cm^{-1}. A number of signals are also found at 1424, 1387, 1371 (s), 1242 (s) and 1211 cm^{-1}. The negative band at around 1620 cm^{-1} is due to the displacement of water. On desorption these signals are attenuated. No characteristic signals of MP can be detected.

Figure 6-4 shows ATR spectra recorded while flowing MP (10^{-3} M) over Deloxan. No signals originating from dissolved MP can be detected. A band at ca. 1700 cm^{-1} grows in fast accompanied by bands at 1422, 1372 and 1240 cm^{-1}. Other strong signals grow in with time at 1589, 1524, 1447, 1351 and 1304 cm^{-1}, whereas that at 1700 cm^{-1} decreases and then levels off. The time behaviour of the signals at 1700 cm^{-1} and of, for example that at 1524 cm^{-1} shows the typical time behaviour for a consecutive reaction. In Figure 6-5 the absorbance signals at 1700, 1524 and 1750 cm^{-1} are shown as a function of time. The time behaviour indicates that the species associated with the signal at 1700 cm^{-1} is transformed to the species associated with the signal

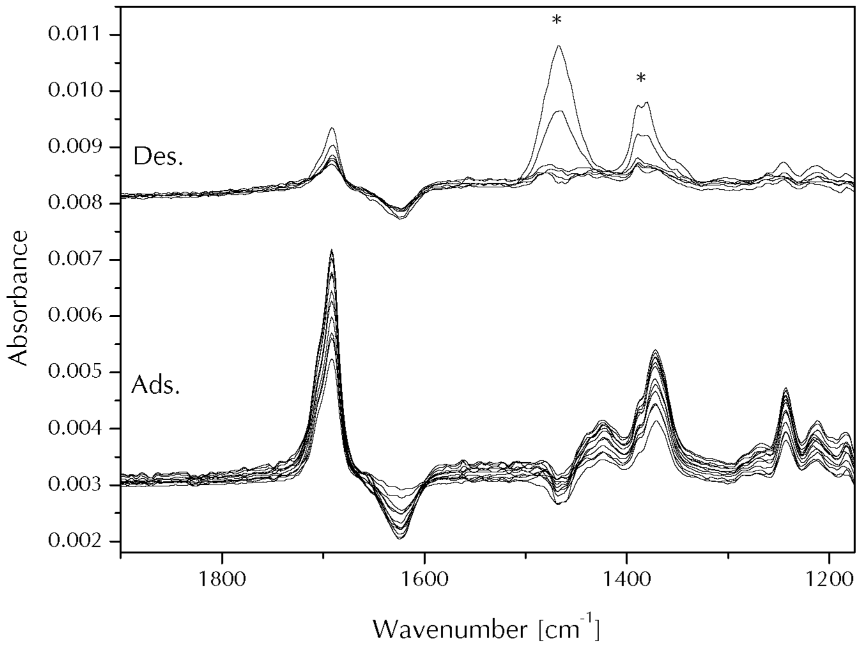

Fig. 6-3: ATR spectra as a function of time recorded while flowing MP at 10^{-3} M in hexane over SiO_2. Asterisks indicate uncompensated contribution from the solvent.

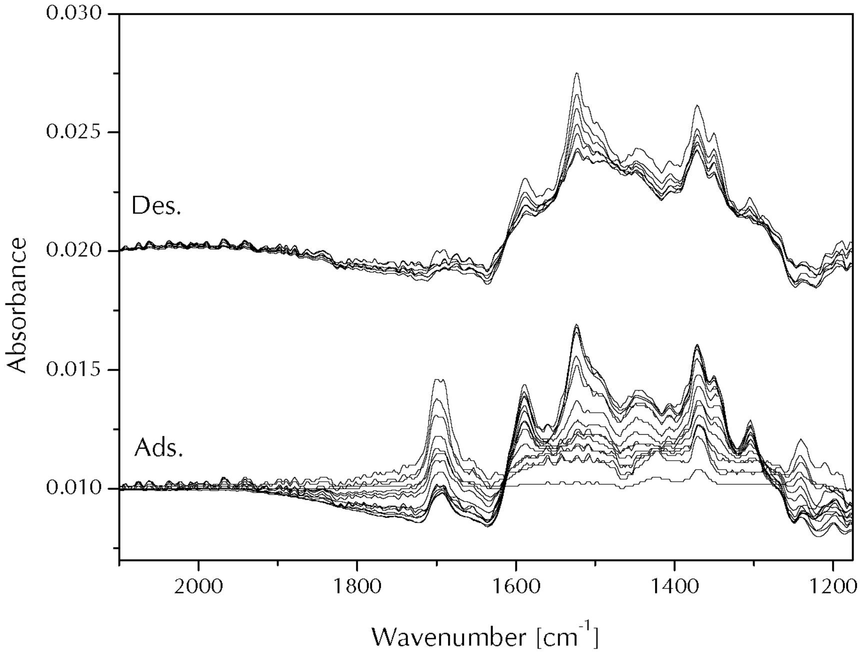

Fig. 6-4: ATR spectra as a function of time recorded while flowing MP at 10^{-3} M in hexane over Deloxan.

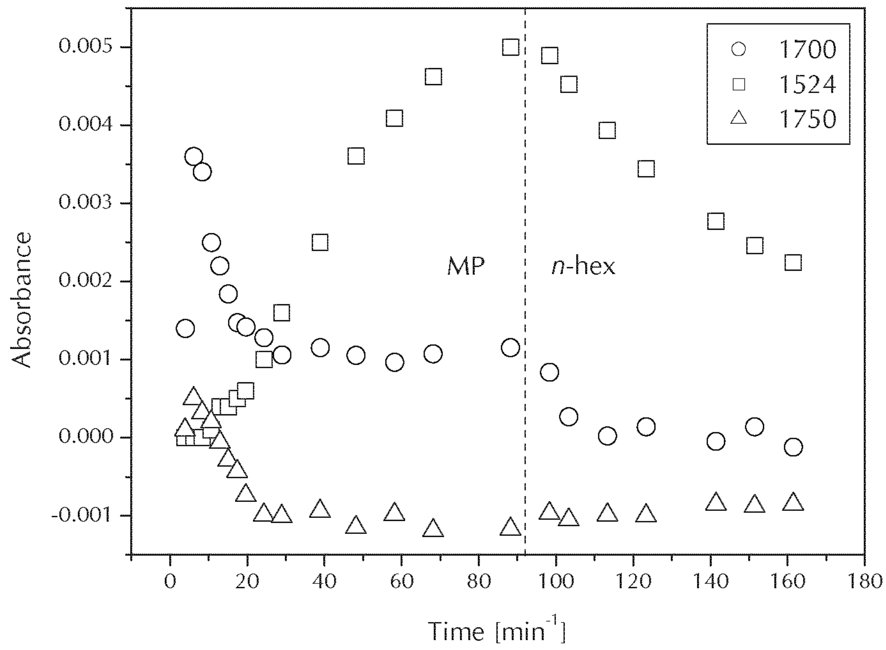

Fig. 6-5: Time dependence of the signals at 1700, 1524 and 1750 cm^{-1} for the experiment depicted in Figure 6-4.

at 1524 cm^{-1} or that the latter species displaces the former from the surface. A very broad negative signal centred at around 1700 cm^{-1} starts to show up when the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1} grow. The time behaviour of this band is also given in Figure 6-5 (absorbance at 1750 cm^{-1}). This signal is likely associated with hydronium ions.

The characteristic band at about 1700 cm^{-1} in Figure 6-3 and Figure 6-4 shows the presence of a carbonyl compound. A possible candidate is acetone. Enol ethers such as MP are readily hydrolyzed by acids [157], resulting in a carbonyl compound and an alcohol. In the case of MP hydrolysis this results in acetone and methanol. Figure 6-6 shows the ATR spectra recorded when contacting a 10^{-3} M solution of acetone on (a) SiO_2 and (b) Deloxan. On SiO_2, signals are observed at 1693, 1423, 1369 and 1242 cm^{-1} in the spectral region above 1200 cm^{-1}. The signal at about 1693 cm^{-1}, representing the stretching vibration of the carbonyl group of acetone is composed of two overlapping bands. Since acetone absorbs at 1722 cm^{-1} in n-hexane the signal at 1693 cm^{-1} is assigned to hydrogen-bonded acetone. It has been reported that acetone shows two signals for the C=O stretching vibration on SiO_2 [158]. The exis-

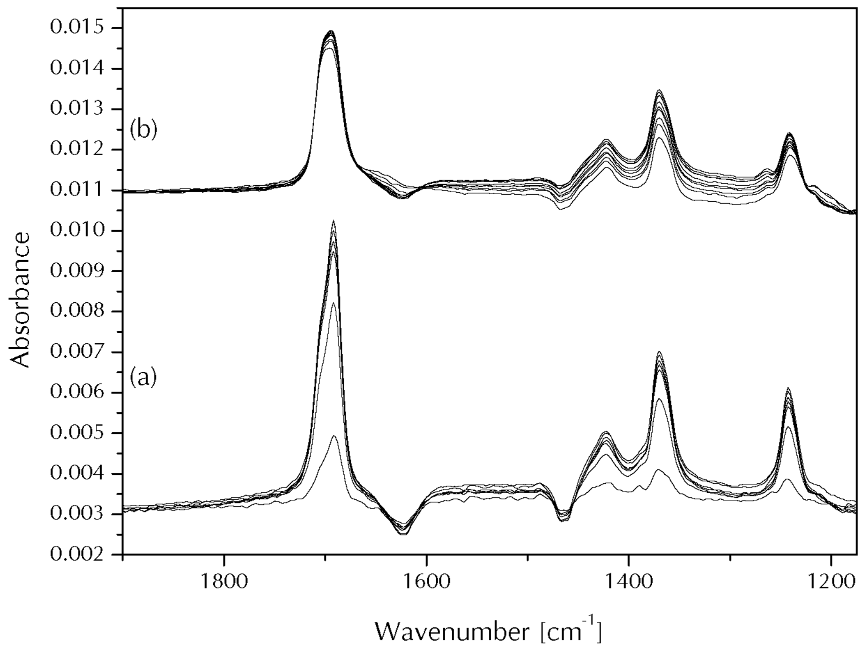

Fig. 6-6: ATR spectra of acetone adsorption on (a) SiO_2 and (b) Deloxan from a 10^{-3} M solution in hexane as function of time.

tence of the two signals has been attributed to the presence of two types of silanol groups, i.e. isolated and grouped. On Deloxan, similar frequencies are found for the characteristic signals of acetone. A slight difference is observed for the shape of the C=O signal: On Deloxan the high and low frequency components of the carbonyl stretching band have similar intensity, whereas on SiO_2 the low frequency component is stronger. For acetone adsorbed on zeolites it was shown that the carbonyl vibration shifts depending on the adsorption site. A frequency of 1700 - 1705 cm^{-1} is expected for acetone bound to SiOH groups, of 1690 - 1702 cm^{-1} for acetone on Lewis sites and of 1655 - 1682 cm^{-1} for acetone on Brønsted sites [159]. The weak band at around 1650 cm^{-1} may be attributed to a small fraction of acetone bound to Brønsted sites. The band is partly overlapped by the negative signal due to desorption of water.

Comparison of Figure 6-3 and Figure 6-4 with Figure 6-6 confirms that acetone is formed upon contacting MP with SiO_2 and Deloxan. In Table 6-2 vibrational frequencies observed when contacting SiO_2 and Deloxan, respectively, with MP and acetone are compared. Moreover, if acetone is admitted to

Table 6-2: Observed bands and proposed assignment for acetone and 2-methoxypropene on SiO_2 and Deloxan.

Acetone Dissolved[a]	 SiO_2	 Deloxan	MP Dissolved[a]	 SiO_2	 Deloxan	 Assignment
1722+sh.↗	1691+sh.↗	1693+sh.↗		1692+sh.↗	1699+sh.↙	$\nu(C=O)$
			1660			$\nu(C=C)$[b]
			1598			overtone $\omega(CH_2)$[b]
					1589	$\nu(C=O)$[c]
					1524	$\nu(C=C)$[c]
			1451			$\delta_{AS}(CCH_3)$[b]
					1447	$\nu(C\text{-}CO)$[c]
1420	1423	1422		1424	1422	$\delta(CH)$
1364	1369	1371		1371	1372	$\delta(CH)$
			1370			$\delta_S(CCH_3)$[b]
					1351	OCH_3
					1304	OCH_3
			1285			$\nu(C\text{-}O)$[b]
1222	1242	1240		1242	1240	$\nu(C\text{-}C)$

[a] In n-hexane.

[b] For the assignment of MP vibration refer to [160, 161]

[c] For this assignments refer to [162].

↗ and ↙ refer to high- and low-energy shoulder, respectively.

the SiO_2 film, on which MP has been previously reacted, similar signals are observed.

On Deloxan acetone formation is possibly acid-catalyzed, whereas the silanol groups may be responsible for the observed reaction on SiO_2. Water adsorbed on the surface is affected by the reaction on both materials. The negative bands observed at around 1650 cm^{-1} in Figure 6-4 and at 1624 cm^{-1} in Figure 6-3 show consumption or displacement of water.

The nature of the further reaction of acetone on Deloxan, evident by the weakening of the signal at ca. 1700 cm^{-1} and the simultaneous increase of the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1}, is less clear. Since MP and acetone are present on the surface, a reaction involving these species is likely. Condensation of acetone [145] can be ruled out, since admission of acetone alone does not lead to the bands mentioned above. Knözinger and coworkers [163] observed signals at 1585, 1523 and 1453 cm^{-1} when adsorbing acetone onto a Y/MgO catalyst at 200 °C. These signals grew in at detriment of the signal due to adsorbed acetone (found at 1711 cm^{-1}). The authors claimed that this behaviour is due to the dimerisation of acetone to diacetone-alcohol (DAA) and the following dehydration to mesityloxide (MSO). In order to check whether the signals observed in Figure 6-4 (1589, 1524, 1447, 1351 and 1304 cm^{-1}) are associated with MSO and DAA, respectively, the two compounds were also adsorbed on Deloxan. Only hydrogen-bonded species could be observed in the ATR spectra and no signal corresponding to the ones observed when admitting MP could be found.

The sulfonic groups of Deloxan promote the further transformation of acetone and MP. This becomes clear when the sulfonic groups are blocked and MP is subsequently contacted with the modified material. An ideal way of blocking acid sites of a catalyst is pyridine adsorption. Hence, pyridine was first adsorbed on Deloxan from a 10^{-3} M solution in hexane. Signals characteristic of both hydrogen-bonded pyridine and pyridinium ions were observed. Then hydrogen-bonded species were totally removed with the following solvent flow. At this point MP was admitted to the surface. Figure 6-7 shows that the signals associated with acetone appear under these conditions, similarly to MP adsorption on SiO_2. The reactions following acetone formation are however suppressed when the acid sites are blocked. This shows that the acid sites are responsible for the further transformations observed after acetone formation.

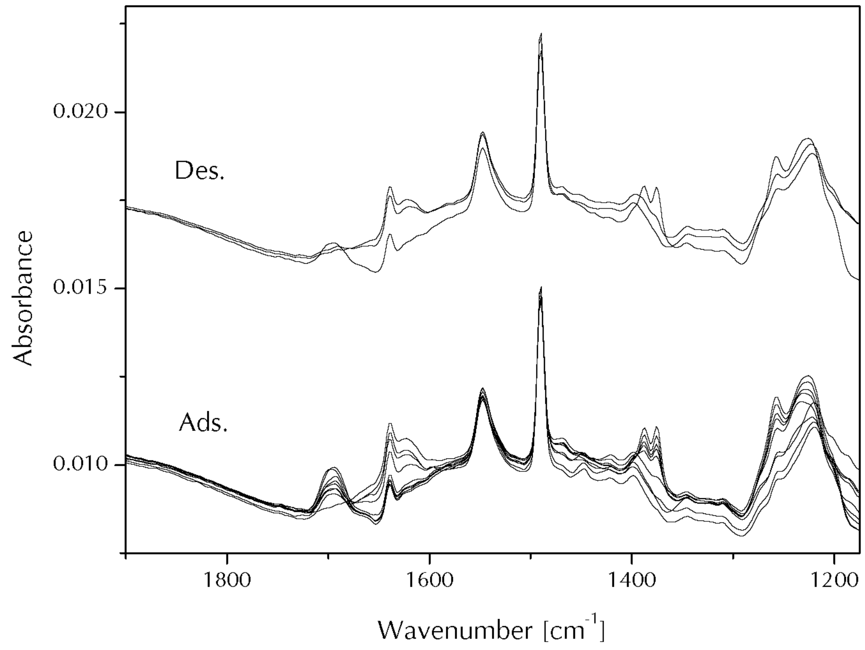

Fig. 6-7: ATR spectra of MP adsorption on pyridine pre-covered Deloxan from a 10^{-3} M solution in hexane as function of time. Pyridine adsorption was performed from a 10^{-2} M solution and after desorbing weakly bound pyridine by flowing neat solvent.

6.2.4 Adsorption of 2,2-Dimethoxypropane on SiO_2 and Deloxan

Hydrolysis of MP to acetone leads to the formation of methanol. The latter can further react with MP to DMP. In order to check whether DMP may be produced when contacting Deloxan with MP, DMP was adsorbed on SiO_2 and Deloxan. The behaviour of DMP on the two materials is similar to that described above for MP. In both cases the signal assigned to acetone is observed at around 1700 cm^{-1} and on Deloxan it disappears again afterwards, whereas the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1} appear. Acetals easily hydrolyze to the corresponding ketone [164]. However, acetals can also be converted to enol ethers [165], i. e. DMP could react back to MP. It is important to note that no adsorbed DMP has been detected when contacting MP with Deloxan. Similarly no adsorbed DMP was observed when admitting dissolved DMP.

6.2.5 Interaction of 2-Methoxypropene with Sulfated and TiO_2-Modified SiO_2

The reaction of MP was also tested on another sulfated catalyst: Sulfated and TiO_2-modified amorphous SiO_2.

Figure 6-8 shows the ATR spectra recorded while contacting this material with MP. Figure 6-9 shows the corresponding time behaviour of the absorbance at 1700, 1524 and 1750 cm^{-1}. As observed in the case of Deloxan, acetone is formed in the early stages of MP adsorption. Further contact leads to the same bands in the 1400-1600 cm^{-1} spectral range that have been described for MP on Deloxan. The time behaviour of the signals at 1700 and 1524 cm^{-1} again show the behaviour of a consecutive reaction.

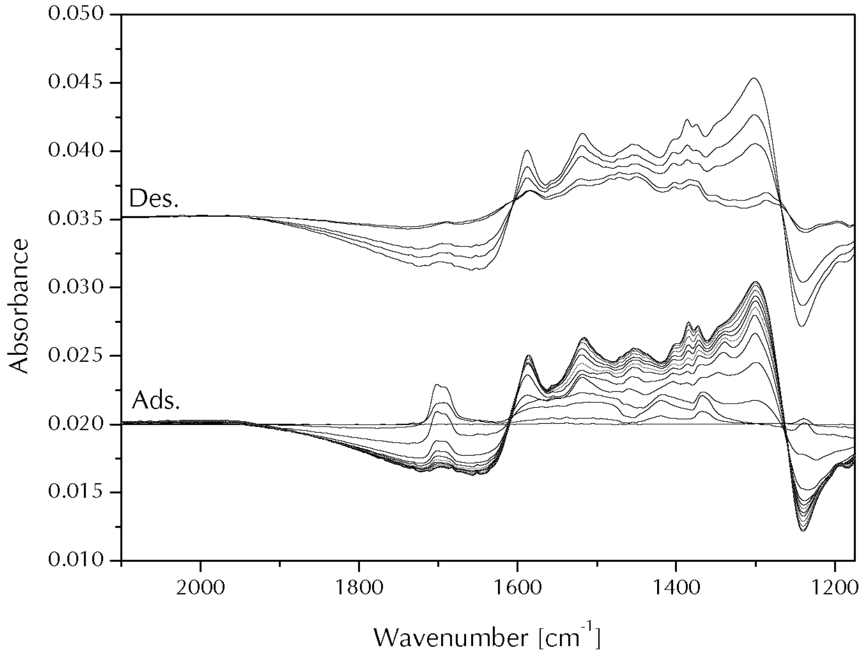

Fig. 6-8: ATR spectra as a function of time recorded while flowing MP 10^{-3} M solution in hexane over sulfated and TiO_2-modified SiO_2.

The acid sites of Deloxan are the responsible for the reactions following hydrolysis of MP to acetone. This has been verified through blocking of these sites by pyridine adsorption. The same strategy was applied to sulfated and

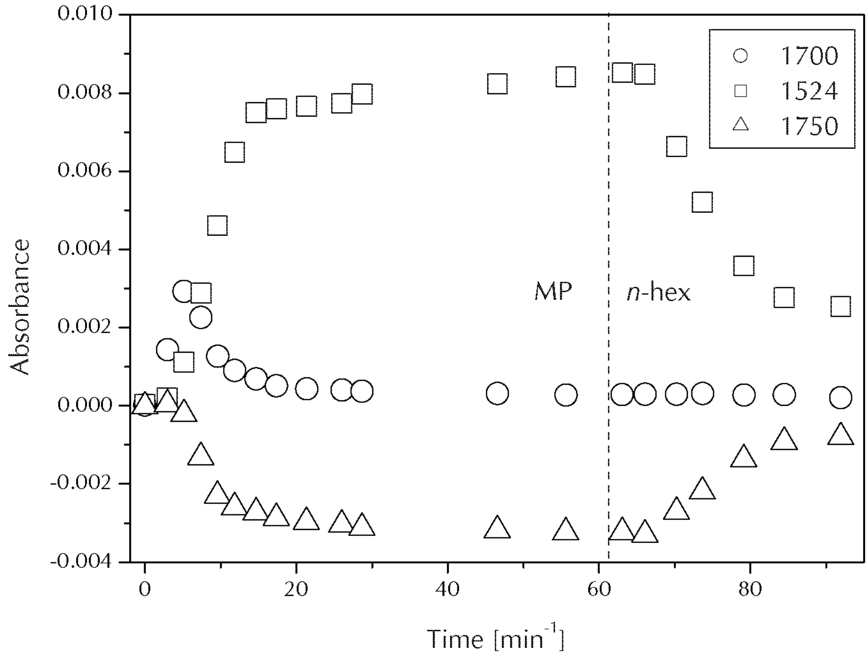

Fig. 6-9: Time dependence of the signals at 1700, 1524 and 1750 cm^{-1} for the experiment depicted in Figure 6-8.

TiO_2-modified SiO_2. Figure 6-10 depicts the ATR spectra of pyridine adsorbed on the sulfated and TiO_2-modified silica from a 10^{-3} M solution in hexane. Signals at 1596, 1578 and 1445 cm^{-1} and at 1638, 1544 and 1488 cm^{-1} indicate formation of HPy and BPy species, respectively. A negative signal at 3701 cm^{-1} suggests that pyridine partly adsorbs on silanol groups, as expected. From the relative intensities of the bands of adsorbed pyridine and pyridinium ion at 1445 and 1550 cm^{-1} a relative concentration C_B/C_L of 8.6 can be estimated. The amount of Brønsted relative to Lewis sites is much higher on the sulfated TiO_2-modified SiO_2 than on Deloxan. When flowing hexane the HPy species desorb from the sulfated TiO_2-modified SiO_2, although very slowly compared to desorption from Deloxan. Acetone is the only product detected when MP is admitted to the thin film, as the doublet at 1702-1692 cm^{-1} suggests. This confirms that also on sulfated and TiO_2-modified SiO_2 Brønsted acid groups are responsible for the reaction of MP.

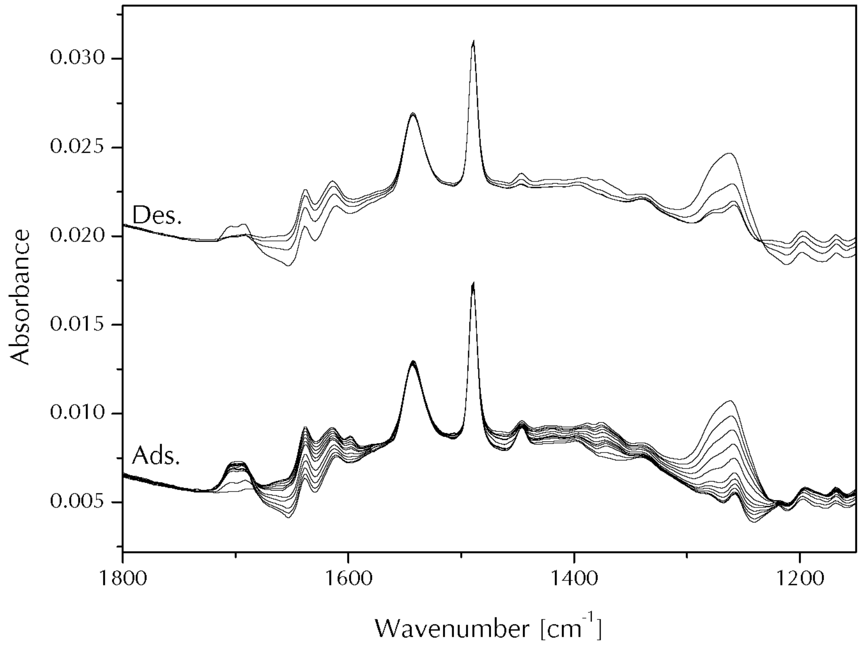

Fig. 6-10: ATR spectra of MP adsorption on pyridine pre-covered sulfated and TiO_2-modified SiO_2 from a 10^{-3} M solution in hexane as function of time. Pyridine adsorption was performed from a 10^{-2} M solution and after desorbing weakly bound pyridine by flowing neat solvent.

6.3 Discussion

Figure 6-11 summarizes the reactions found by ATR spectroscopy. Acetone formation is observed when contacting Deloxan and SiO_2, respectively, with MP (Figure 6-2 and Figure 6-3). Acetone can be formed by hydrolysis of MP, which is corroborated by the negative water bands. The fact that acetone formation is observed on SiO_2 as well as on Deloxan shows that Brønsted acid groups are not a prerequisite for hydrolysis, although hydrolysis of vinyl ethers in homogeneous phase is found to be acid catalyzed involving a proton transfer as the rate determining step [147].

The hydrolysis is fast, since adsorbed MP could be found, neither on SiO_2 nor on Deloxan. Also the signal of the acetone detected at the interface increases fast after admitting MP, as is seen in Figure 6-5. The formed acetone adsorbs on SiOH groups. On Deloxan part of the acetone may furthermore

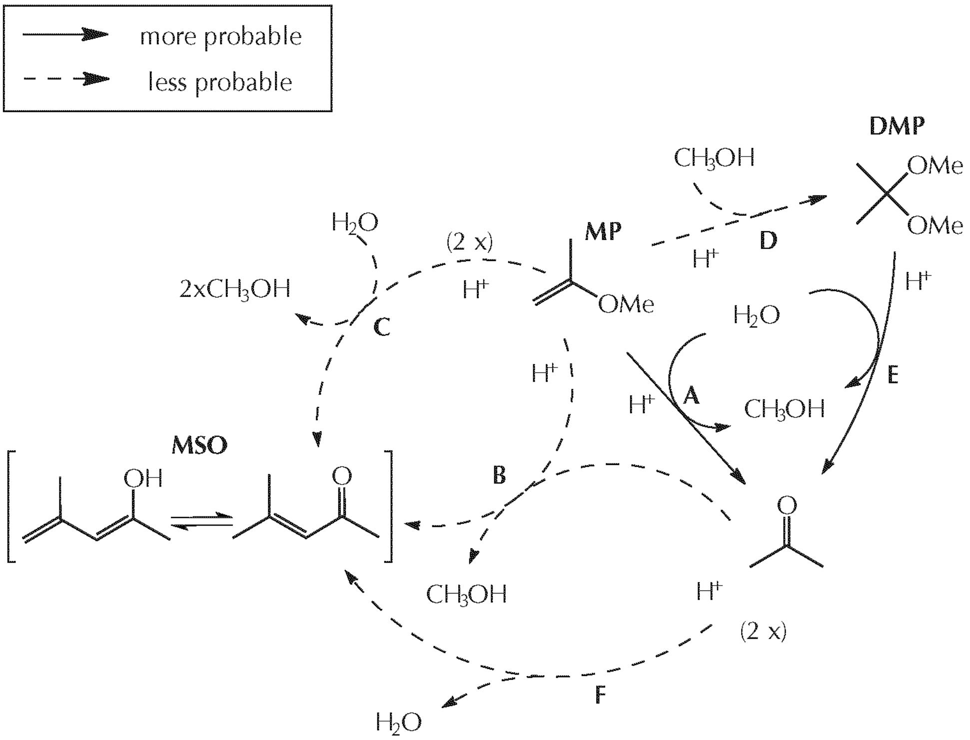

Fig. 6-11: Observed products and reaction pathways of 2-methoxypropene (MP).

interact with the Brønsted acid groups as the weak band at about 1650 cm^{-1} indicates (Figure 6-4). On Deloxan a further transformation is observed leading to a species with characteristic bands at 1589, 1524, 1447, 1351 and 1304 cm^{-1}. Pyridine adsorption clearly shows that this further transformation requires Brønsted acid sites.

Acetone formation by hydrolysis of MP results in methanol. Likely the further transformation observed in the ATR experiments when admitting MP to Deloxan involves MP, acetone or methanol. Acetone dimerisation can be excluded since admittance of acetone alone does not result in the signals observed when admitting MP to Deloxan. The time behaviour of acetone at the interface and of the species associated with the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1} strongly indicates that the transformation yielding the new species is not just a dimerisation of MP. If this were the case one would expect a fast increase of the signals associated with the reaction product from the very beginning of MP admittance. In contrast the signals (e.g. at 1524 cm^{-1}) of the newly formed product grow in retarded with respect to MP admittance and aceton formation, as is clearly seen both on Deloxan and on sulfated and TiO_2-modified SiO_2 (Figure 6-5 and Figure 6-9). In fact the time dependence of the signals strongly indicates that acetone is also involved in this transformation. Based on these considerations the most likely transformation in this respect is therefore an acid catalyzed condensation of acetone and MP, which would yield MSO. On the other hand admittance of MSO (and DAA) to Deloxan did not yield the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1}, which shows that the species giving rise to the signals at 1589 and 1524 cm^{-1} does not correspond to molecular MSO (nor DAA). However, it could be attributed to the enol form of MSO (or DAA). The newly formed species is only slowly desorbing from the interface when flowing neat solvent.

The ATR spectra recorded while admitting MP reveal the behaviour of another species at the interface: The negative broad band at around 1700 cm^{-1} and 1240 cm^{-1} can be assigned to hydronium ions removed from the interface [152, 153]. When admitting MP to Deloxan or sulfated and TiO_2-modified SiO_2 acetone appears before the hydronium ions disappear from the interface, as is seen in Figure 6-5 and Figure 6-9. In the case of sulfated and TiO_2-modified SiO_2 the disappearance of hydronium ions sets in at the same time as the newly formed species appears. This furthermore indicates that acetone formation is not associated with the acid sites whereas the second transformation is. One possible explanation for the observed behaviour is that the acid sites do not only catalyze the second transformation but also serve as adsorption sites for the product. Interestingly, when desorbing the reaction product of the second transformation, the hydronium ion concentration at the interface is largely restored on sulfated and TiO_2-modified SiO_2, whereas it is only to a minor extent on Deloxan, as can be seen from Figure 6-4, Figure 6-5, Figure 6-8 and Figure 6-9.

Methanol can react with MP to form DMP (see Figure 6-11). We do not have direct evidence for the formation of DMP from the spectra. If DMP is formed, it is either fast hydrolyzed to acetone or reacts back to MP and methanol or both. This becomes clear from the experiments where DMP was admitted to SiO_2 or Deloxan. In these experiments acetone is formed. On Deloxan the acetone vanishes again and the same bands appear as are observed when admitting MP on Deloxan. Hence, admission of MP and DMP lead to the same observations in the ATR experiment. The proposal made above based on the time behaviour of the ATR signals that the second observed transformation is a condensation of acetone and MP would indicate that DMP also reacts back to MP and methanol.

The transformations observed with Deloxan are not restricted to this particular material, since they were also observed on sulfated and TiO_2-modified SiO_2. Note that one difference between the two materials is the nature of the Brønsted sites. On Deloxan the Brønsted site are sulfonic acid groups covalently attached to SiO_2 (Figure 6-1) whereas on sulfated and TiO_2-modified SiO_2 the Brønsted sites are sulfuric acid groups adsorbed on TiO_2-modified SiO_2. The two materials have a rather different relative concentration of Lewis and Brønsted sites as pyridine adsorption shows. Also the very different kinetics of pyridine desorption from Lewis sites (O-H groups) indicates different Lewis acid strengths on the two materials. Note that the observed reactions of MP, acetone formation and the transformation resulting in the signals at 1589, 1524, 1447, 1351 and 1304 cm^{-1}, are observed on both materials, although the Brønsted to Lewis acid site ratio and the nature of the Brønsted site is different. However, time behaviour of the acetone signal and the signal associated with the newly formed species (Figure 6-5 and Figure 6-9) is distinctly different on the two materials. First of all the relative ratio between the maximum acetone signal at 1700 cm^{-1} and the signal of the second species at 1524 cm^{-1} is larger on Deloxan than on sulfated and TiO_2-modified SiO_2 (compare Figure 6-5 and Figure 6-9). This is consistent with the observation that on Deloxan the C_B/C_L ratio (ratio of Brønsted to Lewis sites) is smaller and acetone adsorbs primarily on Lewis sites. Also on sulfated and TiO_2-modified SiO_2 the second transformation is faster than on Deloxan as can be seen from the faster decrease of the acetone signal and the faster increase of the signals corresponding to the product of the second transformation. On Deloxan the latter signals do not reach a stable value before 100 min, whereas on sulfated and TiO_2-modified SiO_2 the signal levels off after 15 min. On the other hand the steady state signal of acetone is almost negligible on sulfated and TiO_2-modified SiO_2, whereas it is significant on Deloxan (compare Figure 6-5 and Figure 6-9). A feasible explanation for these observations is the vastly different C_B/C_L ratio (ratio of Brønsted to Lewis sites) on the two materials. Whereas the Lewis sites may be responsible for acetone formation the Brønsted sites promote the subsequent transformation. Due to the smaller C_B/C_L ratio on Deloxan the intermediate aceton is found at higher concentration than on sulfated and TiO_2-modified SiO_2.

6.4 Conclusions

When the vinyl ether 2-methoxypropene (MP) is admitted to heterogeneous acid catalysts complex transformations are observed at the catalytic solid-liquid interface by attenuated total reflection (ATR) infrared spectroscopy. MP hydrolyzes fast to acetone. The latter is observed at the interface immediately after admitting MP. The reaction is so fast that MP itself is not observed. This hydrolysis does not require Brønsted acid sites, and occurs even on pure silica, although vinyl ether hydrolysis is well known to be acid catalyzed in homogeneous phase. However, further transformation requires Brønsted sites. The time dependence of the signals of the intermediate acetone and the ones of the product of this transformation indicate that acetone reacts with MP. The product of this reaction, possibly the enol form of mesityloxide (MSO) adsorbs on the catalyst surface. The relative abundance of Brønsted and Lewis sites determines the concentration of the intermediate acetone on the surface, since its formation is likely due to the Lewis sites whereas its further transformation is due to Brønsted sites on the catalyst. 2,2-dimethoxypropane (DMP) shows the same behaviour on the catalysts as MP, acetone formation and its further transformation, indicating that DMP and MP are easily transformed one into the other on the acid catalysts. ATR infrared spectroscopy turns out to be a viable tool for investigating the transformations at the solid-liquid interface of acid catalysts.

The ATR-investigations clearly indicated that self reactions of MP on the surface impose considerable difficulties in heterogeneous catalysis. These reactions do not occur in homogeneously catalyzed reactions to that extent. MP interacting with the acidic surface is immediately hydrolyzed and thus lost for the desired ketonization reaction. Better mixing conditions in the homogeneous process suppress this competing hydrolysis step and lead to better selectivity.

Additionally, in heterogeneous catalysis dissipation of reaction heat may lead to local overheating at the active sites and thus promotes side reactions. This energy dissipation is much more favourable in well-mixed homogeneous systems (homogeneous catalysis). These seem to be important factors accounting for the less efficient use of reactants (lower selectivity) observed in the heterogeneous catalytic ketonization reactions.

Chapter 7

Outlook

The ketonization of two different α-hydroxyalkynols could be performed for the first time with heterogeneous catalysts. Various aspects were investigated, including a catalyst screening, the influence of reaction parameters on product yield and *in situ* spectroscopy. Still, many questions concerning phase behaviour, adsorption of reactants on catalyst surface and applicability of "supercritical" solvents remain unsolved.

Studies in a high pressure reactor equipped with a glass window could bring a deeper insight in phase behaviour during the ketonization reaction. Especially the relatively unsimilar reactants of the observed DLL-ketonization reaction (large differences in chain length and boiling points of DLL and MP) are sources of possible uncertainties concerning presence in different phases.

Additional studies about usability of "supercritical" solvents should also be carried out in an autoclave with a glass window, to confirm the assumption that the "supercritical" fluid solves the reactants better than a conventional solvent. Whereas the use of "$scCO_2$" as solvent did not prove to be more efficient than a conventional solvent in MB-ketonization, DLL-ketonization with "$scCO_2$" as solvent was much more successful. Possible reasons for these differences could also be investigated in a reactor with a glass window. Even experiments with other "SCFs" should be taken into account.

Another aspect of further studies would be the analysis of catalyst surface residues. During reaction, polymerization reactions of MP produced carbonaceous residues on the catalyst surface. The amount of product formation was highly dependent on different catalyst properties, especially on acidity. Investigations of various catalyst samples with FTIR (before and after catalytic reaction) could reduce uncertainties about influence of these residues on catalyst activities and selectivities. Experiments in the ATR-IR-system with other catalysts could also answer questions about crucial properties of catalysts to catalyze the ketonization reactions efficiently.

Finally, to test additional ketonization reactants with heterogeneous catalysts, that were found to be suitable for the reactions presented in this work, could be interesting.

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Appendix

Additional Investigations of DLL-Ketonization Reaction

On the following pages, a few additional experiments in the field of the continuously catalyzed DLL-ketonization will shortly be discussed, which did not fit in the context of the other chapters. Mainly investigations of in situ treatment of the catalyst and influence of feed flow changes were the points of interest.

Table A-1: Influence of catalyst-flushing with pressurized air. Succeeding actions: longterm treatment at standard conditions (40 h) (sampling "longterm1"); flushing of reactor (for 1 h, 2 bar); standard experiment (4 h) (sampling "after flushing with air").

	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$[%]	$S_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$[%]	$Y_{C13AK, DLL}$ [%]
longterm1	62.2	52.9	31.1	97.3	19.4	51.5
after flushing with air	66.7	54.3	32.1	94.7	21.4	51.5

Table A-1 shows the results of an experiment in which 9.4 g Deloxan ASP I/9 were used for 40 h at standard conditions (see Chapter 2.1). The same catalyst, immediately after taking samples ("longterm1"), was flushed with air for 1 h at 2 bar and 110 °C without opening the reactor before. After this treatment with pressurized air, a standard experiment was carried out (4 h at standard conditions), again without opening the reactor between reaction steps. Samples were taken ("after flushing with air") and, as can be seen in Table A-1, no significant change in activity or selectivity could be observed between untreated and flushed catalyst. This experiment proved that contact with air had no marked influence on catalyst performance.

Corresponding to the experiment described before, an experiment was carried out with catalyst flushing with CO_2 at 50 bar instead of pressurized air at 2 bar. The results in Table A-2 show a similar behaviour as when flushing with air. Only MP-conversions differ slightly between samples from before ("longterm2") and after flushing with CO_2 ("after CO_2 flushing 1").

Table A-2: Influence of catalyst-flushing with CO_2 at 50 bar for 1 h. Succeeding actions: longterm treatment at standard conditions (40 h) (sampling "longterm2"); flushing of reactor (for 1 h, 50 bar); standard experiment (4 h) (sampling "after CO_2 flushing 1").

	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$ [%]	$S_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]
longterm2	61.8	49.6	27.6	92.0	17.1	45.6
after CO_2 flushing 1	56.3	47.8	29.0	92.8	16.3	44.4

Also results for catalyst flushing with CO_2 at 90 bar, as presented in Table A-3, did not show large differences in catalyst performance. Here only selectivity to C13AK related to DLL increased whereas selectivity to C13AK related to MP slightly decreased (from "longterm3" to "after CO_2 flushing 2").

A possible interpretation for the similarity of the experimental results with different flushing methods of the catalyst lies in the relatively long experiment time of 4 h after the flushing event. Possible cleaning or altering of the catalyst surface by flushing with gases at different pressures, is probably undone by reaction conditions during the next 4 h. After all, even after more than 40 h on stream, catalyst performance remains at a high level and can not be altered by flushing the catalyst with different gases at different pressures.

To determine the influence of flow changes on the catalyst activity of a sample of Deloxan ASP I/9, an experiment was carried out as described hereafter: 9.4 g Deloxan ASP I/9 was treated for 40 h at standard conditions. After taking samples ("longterm4"), total flow was increased to 1.41 ml min^{-1}. 4 h

Table A-3: Influence of catalyst-flushing with CO_2 at 90 bar for 1 h. Succeeding actions: longterm treatment at standard conditions (40 h) (sampling “longterm3”); flushing of reactor (for 1 h, 90 bar); standard experiment (4 h) (sampling “after CO_2 flushing 2”).

	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$ [%]	$S_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]
longterm3	57.4	55.5	30.7	86.8	17.6	48.1
after CO_2 flushing 2	59.1	53.9	28.5	93.2	16.8	50.3

later, samples were taken (“high flow”) and then total flow again set to standard flow. Finally, samples were taken after 4 h (“low flow”).

Table A-4: Influence of change in flow rate. Succeeding actions: longterm treatment at standard conditions (40 h) (sampling “longterm4”); standard experiment with higher flow (4 h) (sampling “high flow”); standard experiment (4 h) (sampling “low flow”).

	flow rate [ml min^{-1}]	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$ [%]	$S_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]
longterm4	0.6	55.8	55.2	29.9	81.7	16.7	45.1
high flow	1.41	38.1	43.6	35.6	88.6	13.5	38.6
low flow	0.6	57.4	55.5	30.7	86.8	17.6	48.1

Results in Table A-4 prove that the flow change does not, as could also be observed in flushing experiments, alter catalyst performance. Results from “longterm4” and “low flow” were almost the same (higher MP-conversion and higher C13AK-selectivity (related to DLL) for “low flow”). As could be expected, the higher flow resulted in lower conversion (shorter residence time).

Nafion Experiments

Catalytic tests for DLL-ketonization with three different Nafion types were performed with the following catalysts:

Table A-5: DLL-ketonization with Nafion-catalysts. Conditions: 50 bar, 110 °C, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}.

Catalyst	LHSV [h^{-1}]	X_{MP} [%]	X_{DLL} [%]	$S_{C13AK, MP}$ [%]	$S_{C13AK, DLL}$ [%]	$Y_{C13AK, MP}$ [%]	$Y_{C13AK, DLL}$ [%]	$Y_{ETTP, DLL}$ [%]
4 g Nafion/SiO_2 Engelhard	3.6	97.3	52.4	0.2	1.1	0.2	0.6	6.9
2 g Nafion/SiO_2 Engelhard	7.2	87.9	27.3	0.5	4.9	0.5	1.3	3.5
4 g Nafion/SiO_2 Engelhard / 8 g Alumina	3.6	99.0	60.6	0.0	0.0	0.0	0.0	0.7
4 g Nafion/NR50	13.8	99.2	75.2	0.0	0.0	0.0	0.0	1.5
4 g Nafion/NR50 / 4 g Alumina	13.8	92.3	62.3	0.0	0.0	0.0	0.0	5.0
0.2 ml methanol min^{-1}	1.2	72.9	3.6	0.0	0.0	0.0	0.0	0.0
0.01 ml Nafion 117 per ml methanol (0.2 ml min^{-1})	1.2	83.6	22.5	0.0	0.0	0.0	0.0	0.0
0.1 ml Nafion 117 per ml methanol (0.2 ml min^{-1})	1.2	83.3	9.3	0.0	0.0	0.0	0.0	0.0

Nafion/SiO_2 (Engelhard SAC-13, Nafion supported on silica; "needles" with a diameter of 1-2 mm and a length of 3-12 mm), Nafion NR 50 (Fluka, H^+-form, 7-9 mesh), Nafion 117 Solution (Fluka, purum, ~5 % in a mixture of lower aliphatic alcohols and water) and alumina (Engelhard, for mixtures with catalysts to prevent overheating in the reactor) were used as received.

Table A-5 shows all the results with these catalysts used for catalytic experiments in the continuous flow reactor system (at standard conditions).

Although all catalysts showed high conversions for MP and moderate to high conversions for DLL, none of them led to selective reactions to C13AK. Only low yields of ETTP (related to DLL) could be observed with Nafion/SiO_2 and Nafion NR50 mixed with alumina.

Finally, experiments to determine the influence of temperature on DLL-ketonization with Nafion/SiO_2 were carried out. Figure A-1 gives the corresponding results, whereas at none of the tested temperatures C13AK could be detected. The rise in temperature led to a small decrease of MP-conversion that was compensated by a large increase in DLL-conversion. Whereas MP at low temperature mostly reacted with itself, at higher temperature reactions with DLL became more important. On the other hand, at higher temperature more ETTP had been formed by rearrangement of DLL that did not react with MP.

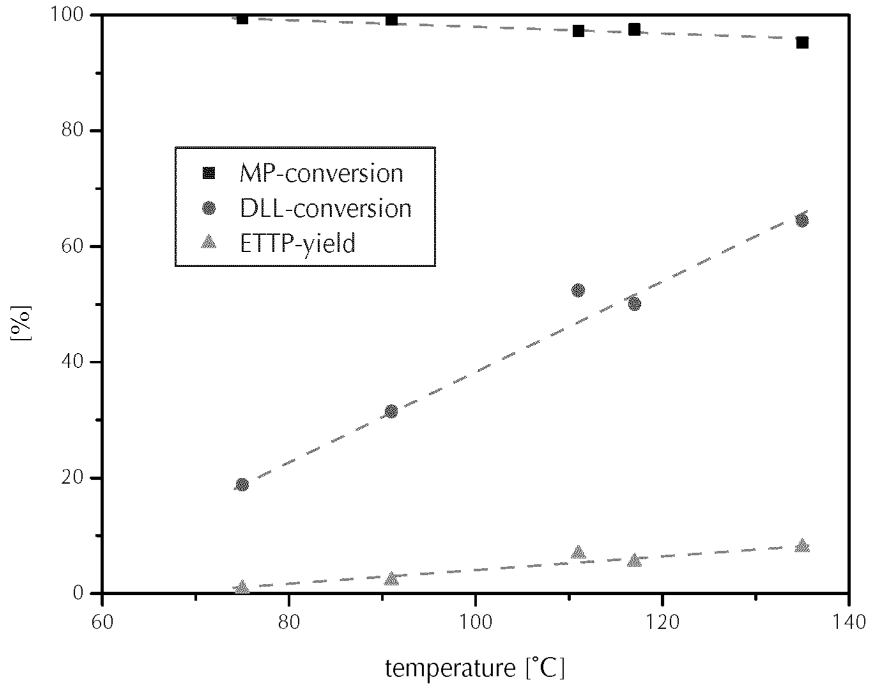

Fig. A-1: Influence of temperature on MP-conversion, DLL-conversion and yield of ETTP (related to DLL). Conditions: 50 bar, molar ratio MP/DLL=3, 0.4 ml MP min^{-1}, 0.2 ml DLL min^{-1}, 4 g Nafion/SiO_2 Engelhard catalyst, no catalyst conditioning. Dashed lines are drawn as a guide for the eyes.

None of the tested Nafion catalysts showed reasonable applicability for catalyzing DLL-reactions to the desired products C13AK or ETTP.

List of Publications

The following list summarizes publications which are based on this thesis. The pertinent chapters of this thesis, which are the source of the publications, are given in brackets. The third publication in this list was published during the thesis but covers another research topic.

Papers

"Interactions of a vinyl ether with acid-modified silica-based catalyst studied by ATR-IR spectroscopy"
D. Ferri, S. Frauchiger, Th. Bürgi, A. Baiker, *Journal of Catalysis*, (to be submitted)
(Chapter 6)

"Continuous Saucy-Marbet ketonization reactions in a fixed-bed reactor"
S. Frauchiger, W. Bonrath, H. Lansink Rotgerink, A. Baiker, *Applied Catalysis A: General* (to be submitted)
(Chapters 3 and 4)

"Restructuring during pretreatment of platinum/alumina for enantioselective hydrogenation"
T. Mallat, S. Frauchiger, P. J. Kooyman, M. Schürch, A. Baiker, *Catalysis Letters* **63**, 121-126 1999

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