Heterogeneous Catalysis in the different Reactor Types on the Examples of Ethyl Benzene to Styrene, Methane Dehydroaromatization and Propylene Carbonate/Methanol Transesterification

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

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Tag der mündlichen Prüfung: 09.07.2009

Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar.
This work was carried out at the chair for Technical Chemistry and Heterogeneous Catalysis of RWTH Aachen, Germany, between January 2004 and December 2006.

I would like to acknowledge many people for helping me during my doctoral work. Especially I wish to thank my advisor, Prof. Dr. Wolfgang Hölderich, for his generous time and commitment. Throughout my doctoral work he encouraged me to develop independent way of thinking and research skills. He continually stimulated my analytical thinking and greatly assisted me with scientific writing.

I thank my second examiner Prof. Dr. Modigell for taking on the task of reviewing this thesis. I thank my third examiner Prof. Dr. Raabe for a friendly participation on the doctoral examination.

I thank Prof. Dr. Weinhold for taking on the task to be a chairman at the examination.

Also I thank DOW Chemicals, ENI Technology and COST Program of the European Union for the financial support during performing this work.

This dissertation would not have been possible without the technical support of the analytic team. Mrs. E. Biener, Mrs. H. Fickers-Boltz, Mrs. M. Naegler, Mrs. N. Mager, Mr. M.Gilliam and Mr. Vaessen are greatly appreciated for the competent support and nice work atmosphere. I am extremely grateful for the assistance and advices I received from Dr. John Niederer and Dr. Michael Valkenberg.

I extend many thanks to all my colleagues and friends, who provided very nice and friendly atmosphere and supported me with advices and actions, especially Hans Schuster, Christophe Duquenne, Jose-Maria Menendez-Torre, Sergio Sabater, Rani Jha, Philipp Klement, Stefan Kujath, Adrian Crossman and many other people.

Finally, I would like to thank my family. I am especially grateful to my mother who supported and encouraged me over years. I thank my wife Elena who was constant source of support and enthusiasm.

Of course, despite all the assistance provided by Prof. Dr. Hölderich and others, I alone remain responsible for the content of the following, including any errors or omissions which may unintentionally remain.
To my family
**Abbreviations used:**

BET – Brunauer, Emmett and Teller, surface area and pore size distribution analysis
DMC – Dimethyl Carbonate
DMS – Dimethyl Sulfate
DPC – Diphenyl Carbonate
DSC – Differential Scanning Calorimetry
DTG – Differential Thermogravimetry
EC – Ethylene Carbonate
EG – Ethylene Glycol
EO – Ethylene Oxide
GC – Gas Chromatography
GC-MS – Gas Chromatography with Mass Spectrometry analysis
GTL – Gas To Liquids
HEMC – HydroxyEthyl Methyl Carbonate
HPMC – HydroxyPropyl Methyl Carbonate
ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrophotometry
MDA – Methane DehydroAromatization
MeOH – Methanol
MFV – Minimal Fluidization Velocity
PC – Propylene Carbonate
PG – Propylene Glycol
PhOH – Phenol
PO – Propylene Oxide
TGA – Thermogravimetric Analysis
TOS – Time On Stream
VHSV – Volume Hourly Space Velocity
WHHSV – Weight Hourly Space Velocity
XRD – X-Ray Diffraction analysis
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1 Problem

Within the framework of the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992 and ten years later in 2002 in the „Johannesburg Declaration on Sustainable Development“ it was agreed that the protection of the environment as well as social and economic development are fundamental to sustainable development [1]. Among other things it was decided to minimize the environmentally harmful effect of the chemical industry.

The problem of sustainable development was recognized by the scientific society and a concept of “green chemistry” was born. Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

Paul Anastas, and John C. Warner developed 12 principles of green chemistry [2], which help to explain what the definition means in practice. The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environmentally benign solvents where ever possible;
- the design of energy efficient processes;
- the best form of waste disposal, aiming not to create it in the first place.

Attempts are being made not only to quantify the greenness of a chemical process but also to evaluate it in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification. In one quantitative study [3], the reduction of nitrobenzene to aniline receives 64 points out of 100 marking it as an acceptable synthesis overall whereas a synthesis of an amide using HMDS (Hexamethyldisilizane) is only described as adequate with combined 32 points.

Technical progress and environment-aware policies set a variety of challenges that make “green solutions” economically attractive. The development of new green processes is unthinkable without use of new effective catalytic systems, primarily heterogeneous.
One of the objectives of this work is to find the way to produce the “green” reagent, dimethyl carbonate (DMC), through transesterification of propylene carbonate (PC) and methanol in the vapor phase. The reaction conditions and the catalyst preparation procedure have to be optimized. The importance of DMC for the development of variety of green syntheses is widely described, e.g. [4, 5, 6, 7, 8, 9, 10, 11, 12].

Another environmental problem should be considered in this work. During crude oil production considerable amount of associated gas is coming out. Due to the difficulties of its use – primary because of the transportation problem – it is just burning out on the wells. This leads to the enormous loss of the energy. The share of flared gas in total gas output varies among main oil-producing regions and nations. According to various estimates around 10-13 bcf (approx. 0.28-0.37 billion m$^3$) of associated gas is flared daily in the world [13]. With the growing share of natural gas in global energy consumption and moreover the growing environmental problems, there is increasingly higher interest in associated gas utilization issues. One of the approaches to utilize the associated gas is the direct conversion of methane to the liquid hydrocarbons like benzene and toluene. Molybdenum loaded HZSM-5 was suggested as a suitable catalyst for this reaction. In this work investigations of Mo/HZSM-5 catalyst for the heterogeneous dehydroaromatization of methane have to be done. Comparison of fixed and fluidized bed reactors as well as influence of different factors has to be investigated and optimal conditions for performing of the reaction have to be found.

Furthermore some problems of a new route to styrene production as developed by DOW Co. have to be investigated. During the operation of a plant some questions of the reaction performing appeared. It concerns e.g. source of the oxygen in the reaction and its dependence from the gas residence times and temperature. Also the influence of the ethane and water presence in the feed on the catalyst activity has to be investigated. The reactions have to be performed heterogeneously in a riser reactor.

Different types of reactors for heterogeneous catalysis have to be applied in this work – fixed and fluidized bed reactors as well as a riser reactor (which is a modification of the fluidized bed reactor).
2 General Part

2.1 Catalysis

Catalysis is the acceleration (increase in reaction rate) of a chemical reaction by means of a substance, called catalyst, which is itself not consumed by the overall reaction. A catalyst decreases the activation energy of a chemical reaction. Catalysts participate in reactions but are neither reactants nor products of the reaction they catalyze. An exception is the process of autocatalysis where the product of a reaction helps to accelerate the same reaction. They work by providing an alternative pathway for the reaction to occur, thus reducing the activation energy and increasing the reaction rate.

The phrase “catalysis” was coined by Jöns Jakob Berzelius in 1835 who was the first to note that certain chemicals speed up a reaction. Other early chemists involved in catalysis were Alexander Mitscherlich who in 1831 referred to contact processes and Johann Wolfgang Döbereiner who spoke of contact action and whose lighter based on hydrogen and a platinum sponge became a huge commercial success in the 1820’s.

There are many theories about how catalysis works. They can be divided in three big groups: geometric, electronic and chemical theories. Geometric theories concentrate on the coordination between geometrical configuration of atoms of the catalyst’s active sites and atoms of reactants. Electronic theories say that chemisorption is conditioned by electronic interaction concerned to the charge transfer. Chemical theories consider catalyst as a chemical substance, which forms chemical bonds with reactants in form of transition complex with its following release and forming of reaction products and the catalyst returns in its previous state. This last theory is considered now as most adequate.

Catalysts can be either heterogeneous or homogeneous. Biocatalysts are often seen as a separate group. Heterogeneous catalysts are present in different phases from the reactants, whereas homogeneous catalysts are in the same phase.

Table 1 gives an overview on advantages and disadvantages of each kind of catalysis. Conditioned by this differences special reactor types are used for each type of catalysis. The most usual reactors for homogeneous reactions are continuous or batch tank and tubular reactors with intensive stirring. For heterogeneous reactions most suitable reactor types are fixed and fluidized bed reactors (see also Chapter 2.2).
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<td>Activity</td>
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<td>Diffusion problems</td>
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<td>Reproducibility</td>
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<td>often difficult</td>
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<td>Understanding of reaction mechanism</td>
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<td>Catalysts deactivation</td>
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<td>Catalysts separation</td>
<td>difficult and costly</td>
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<td>Catalysts preparation</td>
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### 2.1.1 Zeolites

Zeolites are crystalline aluminosilicate minerals that have a micro-porous structure. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral that the stones began to dance about as the water evaporated [14]. Using the Greek words, which mean "stone that boils", he called this material zeolite.

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Natural zeolites are formed where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated with varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Synthetic zeolites hold some key advantages over their natural analogue. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures, which do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to
supply zeolites is virtually unlimited. Finally, zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature. Disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts.

Zeolites are three-dimensional, crystalline compounds, which are built from AlO_4 and SiO_4 tetrahedra, each oxygen of which is shared between two tetrahedrons. The net negative charge on the tectosilicate framework is balanced by the incorporation of cations (interchannel cations) in approx. 2 to 10 Å cages or channels. This feature can also be observed in feldspar and feldspathoid minerals. But in contrast to this feldspar and feldspathoid minerals the zeolite aluminosilicate framework contain open cavities and open channels (i.e. they have lower densities) through which ions can be either extracted or introduced.

Their compositions are represented by the structural Formula 1:

$$M_{x/n} (x\text{AlO}_2 \cdot y\text{SiO}_2) \cdot z\text{H}_2\text{O} \quad (1)$$

Where M represents exchangeable interchannel cation (e.g. Na\(^+\), K\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\), Mg\(^{2+}\), Fe\(^{2+}\) or NH\(_4^+\)) and n is the charge on this cation, z is the number of moles of interchannel molecular water, and x and y are the stoichiometric coefficients for AlO\(_2\) and SiO\(_2\) in tetrahedral sites, respectively. The quantity x/n represents the stoichiometry of the interchannel cations, necessary for maintaining charge balance in the tectosilicate lattices of zeolites. An additional feature, which differentiated the zeolites still further from the feldspar and feldspathoid minerals, is the presence of water molecules within the structural channels. These are relatively loosely bound to the framework and cations, and like the cations they can be removed and replaced without disrupting framework bonds (DEER et al. 1992).

There are many classifications and nomenclatures for the zeolites have been suggested. However, as stated by Nickel & Mandarino (1987): “It is probably not desirable to formulate rigid rules to define whether or not a compositional or crystallographic difference is sufficiently large to require a new mineral name, and each new mineral proposal must be considered on its own merits”. So every kind of rules for nomenclature of zeolite minerals should be viewed as guidelines rather than as being rigidly prescriptive.

Currently, three basic classification schemes are used widely for zeolite structures. Two of these are based upon specifically defined aspects of crystal structure, whereas the third has a
more historical basis, placing zeolites with similar properties (e.g. morphology) into the same group (ARMBRUSTER & GUNTER 2001). The first structural classification of zeolites is based on the framework topology, with distinct framework receiving a three-letter code (MEIER et al. 1996). The second structural method for the classification of zeolites is based on a concept termed “secondary building units” (SBU). The primary building unit for zeolites is the tetrahedron and the SBUs are the geometric arrangements of tetrahedra (BRECK 1974, ARMBRUSTER & GUNTER 2001), see Figure 1 [15]. Quite often, these SBUs tend to control the morphology of the zeolites. The third broad classification scheme is similar to the SBU classification of BRECK (1974), except that it includes some historical context of how the zeolites were discovered and named. This scheme uses a combination of zeolite group names which have specific SBUs and is the widely used by geologists.

Furthermore, widely used is follow pore containing materials classification based on the pores size (d): microporous (d < 20 Å), mesoporous (20 Å < d <500 Å) and macroporous (500 Å < d) materials. According to this classification zeolites have mostly microporous and mesoporous character, see Table 2.

Table 2 represents some zeolites, their ring system and pores size.

**Table 2: Ring system and pore size of some zeolites**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Ringsystem</th>
<th>Pore size in Å</th>
<th>Pores size classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>8-Ring</td>
<td>4.1</td>
<td>Microporous</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>10-Ring</td>
<td>5.4 x 5.6 and 5.1 x 5.5</td>
<td>Microporous</td>
</tr>
<tr>
<td>Mordenite</td>
<td>12-Ring</td>
<td>6.7 x 7.0</td>
<td>Microporous</td>
</tr>
<tr>
<td>Faujasite, zeolite X, Y</td>
<td>12-Ring</td>
<td>7.4</td>
<td>Microporous</td>
</tr>
<tr>
<td>Beta</td>
<td>12-Ring</td>
<td>5.5 x 5.5 and 7.6 x 6.4</td>
<td>Microporous</td>
</tr>
<tr>
<td>MCM 41, MCM 48</td>
<td>-</td>
<td>16 to 100</td>
<td>Mesoporous</td>
</tr>
</tbody>
</table>
2.1.1.1 ZSM-5 and Y-zeolites

In the present work zeolites of type ZSM-5 and Y were used intensively. The structure of these zeolites is presented on the Figure 2 and Figure 3. Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, and 6-6. The pore diameter is large at 7.4 Å since the aperture is defined by a 12-member oxygen ring, and leads into a larger cavity of diameter 12 Å. The cavity is surrounded by ten sodalite cages (truncated octahedra) connected on their hexagonal faces. The unit cell is cubic (a = 24.7 Å) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with a Si/Al ratio of 2.43. It thermally decomposes at 793 °C [16,17,18].
Zeolite Y, like zeolite A, is synthesized in a gelling process. Sources of alumina (sodium aluminate) and silica (sodium silicate) are mixed in alkaline (NaOH) aqueous solution to give a gel. The gel is then usually heated to 70-300°C to crystallize the zeolite. The zeolite is present in Na+ form and must be converted to acid form. To prevent disintegration of the structure from acid attack, it is first converted to the NH$_4^+$ form before being converted to acidic form. If a hydrogenation metal such as platinum is needed, it is deposited via impregnation or ion exchange [18].

The most important use of zeolite Y is as a cracking catalyst. It is used in the acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffin into gasoline grade naphtha. Zeolite Y has displaced zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio. It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content of reformulated refinery products [18, 19, 20].

![Figure 2: Pore structure of zeolite Y](image)

ZSM-5 has MFI structure. It has two types of pores, both formed by 10-membered oxygen rings. The first of these pores is straight and elliptical in cross section, the second pores intersect the straight pores at right angles, in a zigzag pattern and are circular in cross section – see Figure 3 (d). This unique two-dimensional pore structure allows a molecule to move from one point in the catalyst to anywhere else in the particle. The large openings are the elliptical, straight pores in ZSM-5.

The ZSM-5 zeolite catalyst is used in the industry for many reactions (at least 31 correspond to the [20]). It’s most famous application is MTG- and MTO-processes as well as isomerization, hydrocracking and aromatization reactions [20].
2.1.1.2 Synthesis and modification of zeolites

There are several types of synthetic zeolites which are formed by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. One of the important process to carry out zeolite synthesis is sol-gel processing. The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as templates used, such as organic amines and organic quaternary ammonium salts. In sol-gel process, other elements (metals, metal oxides) can be easily incorporated. The silicalite sol formed by the hydrothermal method is very stable. Also the ease of scaling up this process makes it a favorite route for zeolite synthesis.

After synthesis zeolites can be modified by different methods, too. Most common are ionic exchange, impregnation, treating by acids, steaming, heating up, deformation and passivation of surface.

The strength and number of acidic sites of zeolite are tunable. The more Al is incorporated in the SiO$_4$ lattice the more acid sites will be present in zeolite. On the other hand the increased number of acidic sites leads to the decreasing of their strength. Therefore Si/Al ratio is a compromise between number and strength of acid sites. Another method is an isomorphous substitution, which is the exchange of central atoms of tetrahedral lattice (Si and Al) by other elements, which have the charge of two, three, four or five. E.g. Al can be substituted by Be, Co, B, Fe, Ga, Cr, Ti; Si by Ge, P.
2.1.1.3 Application of zeolites

The zeolite market showing the different market segments is presented in the Figure 4 [21]. As can be seen, the catalytic application of zeolites is only a small segment of about 8%, but zeolite catalysts contribute 55% to the market on a cash base. The products obtained by using these catalysts have a value, which is several magnitudes higher than that of the catalysts themselves, thus making them extremely important for many processes.

Natural zeolites are mainly used in building construction (cements) or in paper industry (fillers for paper). Other applications of these materials are as cat litter, sewage water treatment and in agriculture or animal nutrition.

Around 90% of processes in the chemical industry use catalysts and around 80% of them are heterogeneously catalyzed. The growth in catalyst sales is increasing at between 5% and 10% per year. More than 40% of all industrial processes are catalyzed by zeolites [20]. Approx. 74 different zeolites are used nowadays for the industrial processes [20]. The world largest catalytic process is FCC process (Fluid Catalytic Cracking), which uses modified Y-zeolite [19, 20].

Catalysis is not the largest market segment of zeolites but it is the most valuable one. Zeolites are very efficient and selective catalysts for various reactions, especially in the petrochemical industry. The selectivity of zeolites is due to the limited pore sizes, which only allow specific molecules either to enter the pores (reactant selectivity – Figure 5) or to leave the pores.
(product selectivity – Figure 6) depending on their size. Furthermore, not every transition state during a reaction might be possible, thus, forcing a reaction only into one direction (restricted transition-state selectivity – Figure 7).

![Figure 5: Reactant selectivity](image1)

![Figure 6: Product selectivity](image2)

![Figure 7: Restricted transition-state selectivity](image3)
2.2 Gas-solid operations

Most of the reactions in this work were performed in gas phase as gas-solid reactions. The Figure 8 represents different fluidization regimes, which are possible in the reactor systems [22].

First regime corresponds to the fixed-bed reactor. In this kind of reactor the gaseous educts are passing through a bed of solid catalyst without making changes on its state. No fluidization occurs in this regime.

Further increase of gaseous reactants amount (increasing of the gas velocity) leads to the “fluidization” of solids. Fluidization converts a bed of solid particles into an expanded, suspended mass that has many properties of a liquid. This mass has zero angle of repose, seeks its own level, and assumes the shape of the containing vessel.

Performing the reaction in a fluidized bed reactor has many advantages against fixed-bed. These are e.g. better contact between solids and gas, better heat transfer over the bed resulting in isothermal conditions.

Table 3 represents comparison of some aspects of fixed and fluidized bed reactors.

Figure 9 shows pressure drop in fluidized bed by increasing of superficial gas velocity [23]. As it can be seen pressure drop increases in the beginning by increasing of gas velocity. After arriving of $U_{mf}$ (minimum fluidization velocity) pressure drop remains constant (in ideal case). Dotted line represents a real behavior of the pressure drop.
### Table 3: Comparison of fixed and fluidized bed reactors

<table>
<thead>
<tr>
<th></th>
<th>Fixed bed</th>
<th>Fluidized bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-solids contact</td>
<td>moderate</td>
<td>very good</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>low (80 to 90 W/m²°C) [24]</td>
<td>high (600 to 1200 W/m²°C) [24]</td>
</tr>
<tr>
<td>Solids and fluids transfer</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Temperature control</td>
<td>difficult</td>
<td>easy</td>
</tr>
<tr>
<td>Regeneration possibility</td>
<td>only batch</td>
<td>continuously possible</td>
</tr>
<tr>
<td>Catalyst attrition and reactor erosion</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Contact times</td>
<td>constant</td>
<td>varied</td>
</tr>
<tr>
<td>Scaling up</td>
<td>easy</td>
<td>difficult</td>
</tr>
</tbody>
</table>

---

**Figure 9: Pressure drop over superficial gas velocity**

Figure 10 represents heat transfer coefficient bed-wall at three different regimes [24]. After changing to the fluidized state, heat transfer coefficient raises rapidly (upper curve on Figure 10), passes a maximum and decreases finally because of the increased bed porosity. The curve below on Figure 10 represents heat transfer in the empty tube at different regimes. As it can be seen the fluidization state allows great heat transfer rates. Furthermore in a fluidized bed reactor it is possible to set very high temperature difference between wall and catalytic bed, than in fixed bed reactor, without significant internal temperature profile in the bed.

1922 Franz Winkler developed fluidized bed reactor for gasification reaction of fine-grained coal (BASF). Since that time fluidized beds are used successfully in a multitude of both catalytic and non-catalytic processes.
Among the catalytic uses are hydrocarbon cracking and re-forming, oxidation of naphthalene to phthalic anhydride, and ammoxidation of propylene to acrylonitrile. A few of the noncatalytic applications are roasting of sulfide ores, coking of petroleum residues, calcination of ores, incineration of sewage sludge, drying, and classification. Considerable effort and interest are now centered in the areas of coal and waste combustion to generate steam [25]. Low temperature combustion of coal and waste in fluidized bed reactor has a number of key advantages against a pulverized combustion approach. Low combustion temperature results in the lower nitrogen oxides content in the flue gas. Also lime can be added to the coal in order to remove sulfur oxide concentration in the exhaust gas. Next advantages of fluidized bed combustion are possibility to expand the quality range of burned coal/lignite and waste, fuel use of big particle size, better slagging and fouling behavior in the boiler, etc.

Further increase of the gas velocity leads to the state when the solid particles are conveyed by gas flow (pneumatic conveying – Figure 8). This extreme case of fluidized bed reactor is called a riser-reactor. This kind of reactor allows reaching very short residence times of educts with catalyst. This can be necessary e.g. in order to avoid side reactions at high temperatures. Most famous riser application is the FCC process [19, 20].
In 1996, world production capacity for styrene was near 19.2 million metric tons per year. Dow Chemical is the world's largest producer with a total capacity of 1.8 million metric tons in the USA, Canada, and Europe [26].

Styrene is used as a monomer to make plastics such as polystyrene (nearly 65% of all styrene), Acrylonitrile Butadiene Styrene (ABS), Expandable Polystyrene (EPS), Unsaturated Polyesters (UPE), Styrene Acrylonitrile (SAN), Methacrylate Butadiene Styrene (MBS), Styrene Butadiene Rubber (SBR), Styrene Isobutadiene (SB Copolymers). These materials are used in rubber, plastic, insulation, fiberglass, pipes, automobile parts, food containers, carpet backing etc.

Many different techniques have been investigated to manufacture styrene. The following methods have been used or seriously considered for commercial production:

1. Dehydrogenation of ethylbenzene;
2. Oxidation of ethylbenzene to ethylbenzene hydroperoxide, which reacts with propylene to give α-phenylethanol and propylene oxide, after which the alcohol is dehydrated to styrene (known as POSM process for Propylene Oxide / Styrene Monomer), see Eq. 1(a,b,c);
3. Oxidative conversion of ethylbenzene to α-phenylethanol via acetophenone and subsequent dehydratation of the alcohol;
4. Side-chain chlorination of ethylbenzene followed by dehydrochlorination, see Eq.1;
5. Side-chain chlorination of ethylbenzene, hydrolysis to the corresponding alcohols, followed by dehydration;
6. Extraction of styrene from pyrolysis-mixture.

The first two methods are the only commercially utilized routes to styrene: dehydrogenation of ethylbenzene accounts for over 90% of the total world production. Methods 4 and 5, involving chlorine, have generally suffered from the high cost of the raw materials and from the chlorinated contaminants in the monomer. Manufacture of styrene directly from petroleum streams (method 6) is depending on the capacity of pyrolysis plants and is very costly and difficult.
The modern manufacturing route to styrene production is the direct catalytic dehydrogenation of ethylbenzene under adiabatic or isothermal conditions—Eq. 2. The typical catalyst is iron oxide based and contains Cr$_2$O$_3$ and a potassium compound (KOH or K$_2$CO$_3$), which act as reaction promoters. The Shell 105 catalyst for example contains 84.3% iron as Fe$_2$O$_3$, 2.4% chromium as Cr$_2$O$_3$ and 13.3% potassium as K$_2$CO$_3$.

This reaction has a heat of reaction of -121 kJ/mol (-29 kcal/mol) [27]. The reaction temperature is around 600-700°C. Most commercial units operate at conversions of 50-70 wt.%, obtaining selectivity between 88-95 mol.% [28, 29]. The reaction can be performed both isotherm or adiabatic.

Higher temperatures lead to the better conversions but simultaneously higher formation of side products. The significant side products are toluene, benzene, and tar-like products of
styrene polymerization. In order to avoid formation of side products the following operations can be applied [29]:
- performing the reaction at lower pressure (0.1-0.5 bar),
- dilution of reaction mixture by water steam,
- fast cooling of reaction mixture.

Typically, 2.5-3 kg steam is required for each kilogram of ethylbenzene to ensure sufficiently high temperatures throughout the reactor. Steam has several roles in this reaction. It is the source of heat for powering the endothermic reaction and it continuously removes coke that tends to form on the iron oxide catalyst through the water/gas shift reaction shown in Eq.3.

\[
C + 2H_2O \rightarrow CO_2 + 2H_2
\]  

(3)

The potassium promoter on the catalyst is present to enhance this decoking reaction. The steam injected with the reactor feed also dilutes the concentration of the reactant and products in the reaction mixture, shifting the position of chemical equilibrium towards products. The separation of styrene from the remaining ethylbenzene requires tall distillation towers and high reflux ratios, because styrene and ethylbenzene have similar boiling points (145°C for styrene, 136°C for ethylbenzene). Distillation and separation of the crude styrene into product styrene is also complicated by the fact that the temperatures involved in the distillation of styrene initiate the polymerization of the styrene. To prevent this, early styrene plants added elemental sulfur to inhibit the rate of polymerization. During the 1970's additive chemicals consisting of phenol based retarders were developed. The more recently developed free radical inhibitor chemicals are now added prior to distillation. These additives limit the rate of polymerization and allow the separation and purification of the product styrene.

Also many other lab scale routes for styrene production are possible, but that technical realization seems to be difficult due to the polished and refined ethyl benzene dehydrogenation route, described before. Examples of alternative routes are oxyalcylation of benzene by ethane and oxygen, methylation of toluene, co-processing of ethyl benzene and nitrobenzene to styrene and aniline, butadiene cyclodehydrogenation etc. [29, 30]. A typical laboratory synthesis of styrene entails the decarboxylation of cinnamic acid.

This work investigates an alternative process where ethane and ethyl benzene react to styrene, ethene and hydrogen over a catalyst consisting of Ga_2O_3/Pt/K_2O/SiO_2 on alumina [31].
Reaction is shown in Eq. 4. The ethene formed in this dehydrogenation step can be used again for the synthesis of the ethyl benzene, instead of the ethane sourced from oil refining. This process was developed by DOW Chemical [32].

\[
\text{Fe} + \text{C}_{2}\text{H}_{6} \xrightarrow{\text{cat.}} \text{C}_{6}\text{H}_{5} \xrightarrow{\text{C}_{2}\text{H}_{4} + 2\text{H}_{2}} \text{C}_{2}\text{H}_{4} + 2\text{H}_{2}
\]  

(Eq. 4)

The Dow Chemical Company build a pilot plant for performing this reaction. Successful operation of the plant was established. However, some problems occurred during plant working. Increased level of carbon dioxide in the reaction mixture was detected. This problem should be solved in the present work by riser reactor using for the reaction performing.

### 2.4 Methane to aromatics

#### 2.4.1 Introduction

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. Methane's relative abundance and clean burning process makes it a very attractive fuel.

Pure methane is colorless and odorless, but when used commercially is usually mixed with small quantities of odorants, strongly smelling sulfur compounds such as mercaptans to enable the detection of leaks.

Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely. The Table 4 outlining the typical make up of natural gas before it is refined. It can be seen that methane is a main part of natural gas. Other gases contained in natural gas are either contaminants and will be separated and disposed (H\(_2\)S, CO\(_2\)) or they are valuable substances but they must be also separated due to its transportation problem (building of clusters with water at low temperatures – C\(_3\)/C\(_4\)). After
transporting of the gas almost only methane is present in it and very often “methane” is used as a synonym for “natural gas”.

Natural gas is considered “dry” when it is almost pure methane and/or ethane (C₁-C₂), having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present (mostly C₃-C₄ fraction), the natural gas is “wet”. Also natural gas can be ”sweet” or “sour” depends on the hydrogen sulfide/carbon dioxide content.

Methane is a greenhouse gas with a global warming potential of 23 over 100 years [33], i.e. when averaged over 100 years each kg of CH₄ warms the earth 23 times as much as the same mass of CO₂.

Because natural gas is a “gas” and not a liquid or solid, it is difficult to transport from the areas that produce it to the areas that consume it. Natural gas pipelines are economical, but are impractical across oceans. Converting methane to compounds which are more easily transported, such as CNG (Compressed Natural Gas)/LNG (Liquefied Natural Gas) or liquid hydrocarbons is an active area of research.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>70-90%</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>0-20%</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>0-8%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>0-0.2%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>0-5%</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>0-5%</td>
</tr>
<tr>
<td>Rare gases</td>
<td>A, He, Ne, Xe</td>
<td>trace</td>
</tr>
</tbody>
</table>

### 2.4.2 Resources, production and consumption of natural gas

The resources of natural gas are distributed erratically over our planet. Figure 11 [34] represents proved natural gas reserves at the end of 2003. As it can be seen, Middle East with
71 trillion cubic meters has the biggest reserves. Following Europe and Eurasia have 62 trillion m$^3$. Asia and Pacific region as well as Africa have around 13 trillion m$^3$ of gas. And North and South America have 7 trillion m$^3$ of gas respectively. Figure 12 represents relative distribution of the reserves in percent and increase of the proved resources during last 20 years. From year 1985 world natural gas reserves grew up from around 99 up to 180 trillion m$^3$. Because of the relative cheap crude oil in the past no intensive investigations of new natural gas deposits were done. The growing crude oil prices in the recent time and its limited reserves will make natural gas as well as a coal the main energy source in the foreseeable future. Some authors propose that the oil production peak is already arrived and by the end of the first decade of the 21st Century production will have commenced its inevitable long-term decline from resource constraints [35].

Natural gas world production is shown on the Figure 13 [34]. It is clearly to see its growing tendency. Especially South and Central America showed the strongest increase of gas production.

The consumption of the natural gas in North America and Europe was relative stable over last decades as shown on Figure 14 [34]. The intensive economical grow in the recent time of the Asian region as well as of the “rest of the world” is embodied in the increased gas consumption (this grow can be seen more clearly on the oil consumption, but the tendency is clear).
Figure 11: Proved natural gas reserves at the end 2005

Figure 12: Distribution of proved natural gas reserves at the end 2005
2.4.3 Natural gas applications

There are many different applications of natural gas. Main application sectors are power generation, industrial use, residential and commercial use, etc. Figure 15 [36] gives an idea of the proportion of natural gas use per sector and its changes in the last 30 years.
**Industrial use** includes a variety of applications like power generation, heating and cooling processes, waste treatment and incineration, metals preheating (particularly for iron and steel), drying and dehumidification, glass melting, food processing, and fueling industrial boilers. Natural gas may also be used as a feedstock for the manufacturing of a number of chemicals and products. Gases such as butane, ethane, and propane may be extracted from natural gas to be used as a feedstock for such products as fertilizers and pharmaceutical products.

In addition to these uses, there are a number of innovative and industry specific uses of natural gas. Natural gas desiccant systems, which are used for dehumidification, are increasingly popular in the plastics, pharmaceutical, candy, and even recycling industries. In each of these industries, moisture filled air can lead to damage of the end product during its manufacture.

Natural gas absorption systems are also being used extensively in industry to heat and cool water in an efficient, economical, and environmentally sound way. These industrial absorption systems are very similar to those used in commercial settings.

**Other sectors** comprise agricultural commercial and public service, residential and non-specific use. Here should be mentioned many applications of natural gas for heating, cooling and cooking in households, public and private enterprises.

**Transportation:** According to the Natural Gas Vehicle Coalition, there are currently more than 2.5 million Natural Gas Vehicles (NGVs) on the road worldwide. Natural gas vehicles are much cleaner burning than traditionally fueled vehicles. NGVs as they exist today are best suited for large fleets of vehicles that drive many miles a day. Taxicabs, transit and school buses, airport shuttles, construction vehicles, garbage trucks, delivery vehicles, and public works vehicles are all well suited to natural gas fueling. Because these vehicles are centrally maintained and fueled, it is economical and beneficial to convert to natural gas.

Natural gas vehicles have suffered in the past from limited driving range and limited storage space, due to the volume of the CNG that must be carried on-board. However, research is currently underway to develop a mid-sized NGV, with similar range and storage space as its gasoline powered counterpart.
2.4.4 Gas to liquids (GTL) methods

Due to the difficulties of transport, storage and use of the gaseous methane a lot of investigations were devoted its conversion to the liquid hydrocarbons. These methods can be divided into the direct and indirect methods.

**Indirect Methods** that use conversion of methane to carbon monoxide and hydrogen (syngas). This can be realized through three reactions: steaming reforming, dry reforming and partial oxidation. To date, the only large-scale process for natural gas conversion is steam reforming, see Eq. 5.

The first description of a process for the conversion of hydrocarbons with steam was published in 1868 using CaO as a medium, resulting in the formation of CaCO$_3$ and hydrogen [37]. In 1890 Mond and Langer improved the process by using a nickel catalyst [38], and it was subsequently used, in combination with Fischer-Tropsch technology (s. Eq. 6), by Germany in World War II and South Africa during the Apartheid era for the synthesis of chemicals such as fuels and alcohols. The process is highly endothermic and current industrial catalysts are usually based on nickel [39].
Syngas is used for consequently followed synthesis of methanol - see Eq. 7. Methanol can be used for production of variety of valuable products: methyl t-butyl ether, dimethyl ether, gasoline, ethylene etc.

Another way of syngas use is mentioned above Fischer-Tropsch synthesis - see Eq. 6. Different hydrocarbons can be produced over this route depend on the reaction conditions.

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{(Eq. 5)}
\]

\[
nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad \text{(Eq. 6)}
\]

\[
CO + 2H_2 \rightarrow CH_3OH \quad \text{(Eq. 7)}
\]

**GTL Direct Methods** comprise follow possibilities:
- Oxidative coupling of methane to ethylene (OCM);
- Direct oxidation of methane, forming methanol and formaldehyde;
- Non-oxidative direct conversion of methane to aromatics.

Oxidative coupling of methane started in the early 1980s and quickly bloomed from the mid-1980s to the mid-1990s [40]. However, no catalysts could reach a C\textsubscript{2+} yield higher than 25% and selectivity to C\textsubscript{2+} higher than 80%, which are the main criteria for industrial application of the OCM, and the research passion on the topic was gradually weakened.

Continuous direct oxidation of methane to methanol [41, 42] or formaldehyde [43] can be performed with maximum of yields around 8% and 4%, respectively. A batch process giving methanol yield more than 50% was recently described but it still has crucial drawbacks due to the need for a mercury catalyst and the consumption of sulfuric acid, leading to sulfur dioxide which then needs to be converted back to sulfuric acid [44].

Non-oxidative direct conversion of methane to aromatics was observed first time in 1993 [45] and is very promising way to produce aromatics and hydrogen. Industrial use of this route is hindered by low yields and short catalyst service time. This topic will be discussed very intensive in the next chapter.
So, each alternative has its own set of limitations and extensive utilization of methane for the production of fuels and chemicals appears to be near, but current economic uncertainties limit the amount of research activity and the implementation of emerging technologies.

2.4.5 Methane Dehydroaromatization (MDA)

2.4.5.1 Introduction

Since its first observation in 1993 [45], increased interest to MDA is observed. When “methane dehydroaromatization” entered in the program “SciFinder”, a widespread distribution of a number of published papers on this topic over last 12 years appeared (state October 2006) s. Figure 16. Since 1993, a variety of different experimental techniques and procedures have been utilized to maximize conversion to desired aromatics, but despite these efforts, reported conversions have remained low. In addition to this, catalytic performance is hindered by significant deposition of carbonaceous species. These problems inhibit further investigation into the industrial use of catalysts for this reaction.

![Figure 16: Distribution of a number of published papers to the topic “methane dehydroaromatization” over the years](image)

The MDA reaction scheme is shown by the Eq. 8. The main reaction products are aromatics: benzene, toluene and naphthalene. No other aromatics were detected during this work. Some other researchers reported formation of other aromatic products, e.g. xylene and benzaldehyde
The most desired benzene can be produced with high selectivity up to 95 mol.%. The naphthalene follows with 5 to 50 mol.% selectivity and only few percent of the toluene can be produced. Ethane and hydrogen are main gaseous products of this reaction. Presence of small amounts of ethane indirectly indicates the formation of C$_2$-species during reaction. Also traces of ethene could be detected. Strong formation of carboneous deposits on the used catalyst is still a big problem for the industrial application of MDA. The aromatic formation becomes significant at temperatures over around 700°C. An increased temperature favors the reaction rate but causes irreversible deactivation of the catalyst due to the Mo leaching.

$$\text{CH}_4 \xrightarrow{\text{Mo/HZSM-5}} \text{C}_6\text{H}_6 + \text{C}_7\text{H}_{10} + \text{C}_{10}\text{H}_8 + \text{C}_2\text{H}_4 + \text{H}_2 + \text{coke} \quad \text{(Eq. 8)}$$

2.4.5.2 Overview about MDA catalytic systems

Since its first observation in 1993 [45] with Mo/HZSM-5 much research and suggestion in order to improve this catalytic system were done. The investigations were concerned both on the incorporated in the HZSM-5 lattice metal and on the HZSM-5 support itself, as well on the different pretreatment/activation techniques.

For example in [49, 50] authors describe effective use of W/HZSM-5 for MDA. Additional incorporation of Zn (or Mn, La, Zr) improves activity and heat-resistance of catalyst.

Use of Rh/HZSM-5 for MDA was described in [51]. Only hydrogen and coke were found as main reaction products. However, addition of Rh to 6 wt.% Mo/HZSM-5, described in [52], improves the stability of the catalyst at longer TOS (longer than 25h), if hydrogen was used as co-feed (6%).

Promotional effect of Cr was detected in [53]. Much better methane conversion (approx. 12% vs. 8 %) was obtained if Cr/Mo molar ratio of 0.07 instead only Mo was used. Addition of small amount of Ga to Mo/HZSM-5 improves catalytic performance [54]. Yield of C$_2$-C$_{11}$ hydrocarbons increased from 7.84 to 8.96%.
Liu found remarkable increase of naphthalene and benzene formation if Co- and Fe-modified Mo/HZSM-5 was used for MDA [55]. Optimal concentration of these metals was found.

Re/HZSM-5 can be used for MDA at lower temperatures (858K) as shown by Wang et al [56].

In [57] authors studied addition of Pd and Ru to Mo/HZSM-5. Pd leaded to strong formation of polyaromatic species, causing a high deactivation rate. Thereagainst Ru favored stability of the reaction, hindering coke formation.

Conversion of methane over different transition metal ions on HZSM-5 was investigated in [58]. It was detected that the activity decreases in the order: Mo>W>Fe>V>Cr.

Positive effect of silanation of HZSM-5 zeolite support is described in [59, 60]. This kind of pre-treatment can improve both activity and stability of catalyst [59]. Additionally to this selectivity to benzene can be improved greatly (over 90%) [60].

Also another zeolite types can be used for MDA. For example Mo/HMCM-22 is described as high selective benzene formation catalyst for MDA [61] as well as HZSM-11, HZSM-8, HMCM-41, HMCM-22, HMCM-49, H-beta, HY and H-mordenite [62, 63, 64, 65, 66, 67, 68, 69, 70].

2.4.5.3 Reaction mechanism

The exact reaction mechanism is still under debate. It is generally accepted that Mo/HZSM-5 is a bifunctional catalyst [71, 72, 73, 74, 75].

Briefly, the Mo-species are well dispersed on/in HZSM-5 after calcinations and they are reduced by methane in the initial period of reaction to form MoCₓ and/or MoCₓOᵧ species, which are responsible for the activation of C-H bond of methane and formation of C₂Hᵧ species (y<4) [73, 74, 75]. After that, due to the unique channel structure of HZSM-5, together with its Brønsted acid sites and the suitable pore size of 0.53 nm x 0.56 nm, which is close to the kinetic diameter of benzene molecule, aromatization of the C₂ intermediates can
proceed easily [70, 76]. Since either ethylene or ethane aromatization proceed easily in the temperature range 573-873 K over HZSM-5, it is clear, that methane dehydrogenation and dimerization to the C\textsubscript{2} species is the rate-determining process.

Even in the first steps of MDA investigations a very important role of reduced MoC\textsubscript{x}O\textsubscript{y} species was noticed, e.g. [62, 77]. This carbide clusters species have been formed from Mo oxide and/or MoO\textsubscript{x} precursors during the induction period (contact with CH\textsubscript{4} at temperatures about 950-1000 K). MoC\textsubscript{x}O\textsubscript{y} species are proposed to be responsible for the cleavage of C-H bond of methane, first step in the MDA reaction. Different techniques like TGA, TPD, XRD, XPS, XAS, EXAFS, XANES, \textsuperscript{1}H, \textsuperscript{27}Al and \textsuperscript{13}C MAS NMR, FTIR, ISS, HRTEM, EPR, RE2PI et al. were successfully applied in order to detect and characterize this active Mo species.

Mentioned above MoO\textsubscript{x} precursors are formed from Mo during calcination/activation/regeneration period, which is normally done in air/oxygen atmosphere at temperatures about 850 K. Very important observations about this procedure was done by Liu et al. and Iglesia et al. in [73] and [78] respectively. The authors found that during this step Mo species interact with and replace the Brönsted acid sites in the channels of the HZSM-5 zeolite with a stoichiometry of 1:1. Around 18 h of air pretreatment is necessary to complete this process. After that time all of Mo species are associated with the Brönsted acid sites. Important is the fact that only associated Mo species are active in the MDA. Also that observation, that Brönsted acid sites are responsible not only for aromatization of C\textsubscript{2} species, but also for the coke formation plays significant role for creation of effective MDA catalyst.

2.4.5.4 Different techniques to improve MDA

Many different techniques are suggested in order to improve catalysts activity and/or stability, as well as selectivity to desired products like benzene. There are e.g.:

- different routes for catalysts preparation;
- use of different Si/Al ratios of HZSM-5 [79];
- different kinds of catalyst pretreatment (hydrothermal post-synthesis [80], silanation [59, 60], pretreatment with HCl [79], use of different calcination temperatures [81], atmospheres and times [82], steam pretreatment [83]);
- different reaction temperatures [84];
- use of co-feeds such as hydrogen [85], CO₂/CO [84, 86, 87, 88, 89, 90], oxygen [91], dimethyl ether [92], NO [93, 94] etc.;

2.4.5.5 Overview on Methane Dehydroaromatization

Despite much research on this reaction and a number of suggested catalytic systems MDA reaction remain to be performed only in the labor scale. The main reasons for this are the low methane conversions and relative short catalyst service time.

The best catalyst for MDA was reported a Mo/HZSM-5 with the optimum range of Mo loading of 4-6 wt.% [71, 75]. Catalyst is active for MDA at the reaction temperatures above 650°C. The methane conversion grows proportionally to the temperature increase. However, irreversible catalyst deactivation occurs at the temperatures above 800°C. Normally MDA reaction will be performed at 700°C. Mo/HZSM-5 is very selective to the aromatic products – benzene, toluene and naphthalene. Typically no side products can be detected in the reaction mixture (except formed coke). Longer TOS favors better aromatic selectivity.

Catalyst can be regenerated by oxidizing of the formed coke after reaction. Regeneration procedure using hydrogen was suggested also, e.g. [85].

Different kind of catalyst preparation and catalyst pretreatment allow some improving of the catalyst activity but the coking problem is necessarily remaining.
2.5 *Dimethyl Carbonate production*

2.5.1 Dimethyl carbonate and Green Chemistry

A lot of investigations are devoted nowadays to find an effective and simple route to produce a Dimethyl Carbonate (DMC). There are many reasons that make DMC really attractive as a “Green Chemistry” reagent.

First of all DMC is non-toxic for humans and environment and has rapid biodegradability. E.g. its oral LD50 is 13000 mg/kg. Its versatile methylation and carbonylation properties open many routes for clean and effective organic syntheses. Depending on the conditions it can be a very effective methylating agent instead of toxic dimethylsulfate or carboxymethylating agents as substitute for poisonous phosgene, e.g. [95, 96, 97, 98]. Comparison of toxicological properties of these substances is given in Table 5. As it can be seen, compared with phosgene or DMS, DMC has much less toxicity and is not a mutagenic substance.

Also DMC found many applications in other areas: as octane enhancer ((M+R)/2 octane number = 105, high oxygen content of 53 wt.%); as expanding system for polyurethane foams; as lubricant for the cold-rolling of steel, as synthetic lubricant and high-performance functional fluid; as a solvent in a process for deasphalting and demetalling of crude oil residues; as electrolyte in batteries due to the its high dielectric constant etc. [99, 100].

There is few new synthesis routes developed instead of old phosgene route presented in Eq. 9.

\[
2\text{ROH} + \text{COCl}_2 \leftrightarrow (\text{RO})_2\text{CO} + 2\text{HCl} \quad \text{(Eq. 9)}
\]

Eq. 10 represents DMC synthesis route based on Oxidative Carbonilation of alcohols. This reaction can be performed in liquid and gas phase.

\[
2\text{ROH} + \text{CO} + \frac{1}{2}\text{O}_2 \leftrightarrow (\text{RO})_2\text{CO} + \text{H}_2\text{O} \quad \text{(Eq. 10)}
\]

Since 1983 EniChem has an industrial plant in operation to produce DMC via this route in the liquid phase in the presence of copper chloride catalysts [101]. No industrial applications of gas phase catalytic systems are known despite there are many investigations carried out [100].
Another route uses urea and methanol as starting materials as presented in Eq. 11. For example Wang et al. [102] showed up to 30% of DMC yield is obtained by using ZnO as heterogeneous catalyst with high stability and reusability.

\[
2 \text{ROH} + (\text{NH}_2\text{CO}) \leftrightarrow (\text{RO})_2\text{CO} + 2 \text{NH}_3
\]  

(11)

Also it is possible to produce DMC by use of metal carbonate as presented in Eq. 12.

\[
2\text{RBr} + \text{KHCO}_3 \leftrightarrow (\text{RO})_2\text{CO}
\]

(12)

<table>
<thead>
<tr>
<th>Properties</th>
<th>DMC</th>
<th>Phosgene</th>
<th>DMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD 50, oral acute toxicity (rats), g/kg</td>
<td>13,8</td>
<td>N.A.</td>
<td>0.20</td>
</tr>
<tr>
<td>LD 50, acute toxicity per inhalation (rats), mg/l</td>
<td>140 (4h)</td>
<td>16 mg/m³ (75 min); 0.02 mg/l (30 min)</td>
<td>1,5 (4h); 0.05 (Human, 10min)</td>
</tr>
<tr>
<td>Product classification</td>
<td>Slightly toxic</td>
<td>Poisonous gas</td>
<td>Corrosive/Poison</td>
</tr>
<tr>
<td>Mutagenic properties</td>
<td>Negative</td>
<td>N.A.</td>
<td>Mutagenic, Carcinogen (Human suspected)</td>
</tr>
<tr>
<td>Biodegradability (OECD 301 C)</td>
<td>&gt; 90% (28dd)</td>
<td>Rapid hydrolysis</td>
<td>Rapid hydrolysis</td>
</tr>
<tr>
<td>Note</td>
<td>Hazardous Waste</td>
<td>Hazardous Substance</td>
<td>Hazardous Waste</td>
</tr>
</tbody>
</table>

2.5.2 General considerations to the EC/PC and MeOH transesterification

Another interesting method for DMC synthesis is a reaction of epoxides, CO₂ and methanol as illustrated in Eq. 13 and 14. This reaction can be performed as “one pot” synthesis as well as two sequenced reaction steps. The catalysts for first reaction (Eq. 13) are usually effective for the consequent reaction shown in Eq. 14. An important advantage of this route is a coproduction of glycols, which can be used directly (as e.g. cooling agent for engines) or for the synthesis of epoxides and subsequently cyclic carbonates.
DMC and methanol form an azeotrope having a composition DMC*6MeOH (30 wt.% DMC, 70 wt.% MeOH) with boiling point of 63°C at 1 atm. The position of reaction equilibrium in a closed system occurs at the maximum of concentration of this binary azeotrope [103].

\[
\text{RCH}_2CH_2O + \text{CO}_2 \rightarrow \text{RCOC}_3\text{O}
\]  
(Eq. 13)

\[
\text{C}_3\text{O}_5 + 2\text{MeOH} \rightarrow \text{MeO}_2\text{C}_2\text{O} + \text{RCH}_2CH_2OH
\]  
(Eq. 14)

It is known, that reaction of epoxides and CO\(_2\) (Eq. 13) can be performed with a quantitative yield, as reported in e.g. [104].

The transesterification reaction of cyclic carbonates and methanol (Eq. 14) is more difficult to perform due to the unfavorably thermodynamic of the process. Usual solutions for this problem are increasing of the methanol excess and use of special reactors, which continuously remove reaction products (e.g. [105, 106, 107]).

Nature of radical R- (see Eq. 14) has strong influence on the reactions thermodynamic. The longer this radical is, the more steric hindrance occurs. For example Bhanage et al. [108] studied differences in DMC yield of transesterification of ethylene/propylene carbonate with different alcohols. They showed that the use of higher alcohols slightly reduces the DMC yield if ethylene carbonate was used (from 70 mol.% in case of methanol to 45 mol.% in case of butanol). But in case of propylene carbonate DMC yield drops already by using ethanol to 10 mol.% and becomes negligible in case of butanol – around 5 mol.% yield.

Most of the researchers perform this reaction using autoclaves under CO\(_2\) pressure. The reason for this is that CO\(_2\) prevents the decomposition of cyclic carbonate to the epoxide and CO\(_2\), described e.g. in [109].
2.5.3 Reported catalytic systems for EC/PC and Methanol transesterification

A number of different catalytic systems for transesterification of EC/PC and MeOH have been reported.

Knifton and Duranleau [104] described eight classes of catalysts, suitable for transesterification of Ethylene Carbonate (EC) and Methanol. These were:
(a) macroreticular and gel-type exchange resins with tertiary amine groupings bounded to a polymer backbone;
(b) ion-exchange resins with quaternary ammonium functional groups;
(c) zirconium, titanium and tin homogeneous catalysts;
(d) homogeneous Group VB and VIB compounds;
(e) alkali metal silicates on silica;
(f) ammonium-exchanged zeolites such as LZY-82;
(g) acidic resins bearing sulfonic acid and carboxylic acid functional groups;
(h) tertiary phosphine polymer catalysts.

They found that bases are more effective than acids for this reaction. Conversion of EC was typically around 50-60% (MeOH:DMC ratio 4:1), DMC and EG selectivity around 98-99%. Reaction conditions: 60-150°C, 100 psi, tubular steel reactor.

Bayer and DOW patented the use of inorganic base such as alkali metal alkoxide, carbonates or hydroxide etc. as catalyst [110, 111]. Bayer also patented the use of organic base, tertiary amine, as catalyst [112].

Tatsumi et al. [113] described use of titanium silicate molecular sieve, TS-1, exchanged with an aqueous solution of K₂CO₃ as a heterogeneous catalyst for transesterification of ethylene carbonate and methanol. Around 68 % of EC conversion and 57 % DMC yield were reported. Reaction conditions: MeOH:EC molar ratio = 4:1, 89 mg catalyst, 31 mmol EC, 124 mmol MeOH, 3h reaction time.

Man Seok Han et al. [114] made a comparison of the activity of KOH, NaOH, LiOH and K₂CO₃ homogeneous catalysts. LiOH showed the highest activity with 61.94 mol.% EC
conversion and 61.52 mol.% DMC yield. Reaction rate by using of LiOH was $2.538 \times 10^2 (\text{dm}^3/\text{mol})^{0.21}/\text{min}$ at 298 K.

Reaction conditions: MeOH:EC molar ratio = 4:1, 25°C, pressure 50 psig by N$_2$, 0.1 g of catalyst, reaction time 1h.

Jiang et al. [115] reported that follow homogeneous catalysts are active for transesterification of propylene carbonate and methanol: IIA group oxide, IA group hydroxide, carbonate and salt. The optimal reaction conditions were as follows: temp. 333-353K, reaction time 1 h, dosage of catalyst 1.0-2.5%, ratio of allyl carbonate to methanol 1:5.

Watanabe et al. [116] reported about successful use of hydrotalcites for transesterification of ethylene carbonate and MeOH. Especially Mg-Al hydrotalcite-type with low Al concentration in brucite-like layers and high OH- proportion in the interlaced anions gave 70 mol.% of EC conversion and 58 mol.% of DMC yield. Reaction conditions: 89 mg of catalyst, 2.72 g of EC, 3.96 g of MeOH, MeOH:EC molar ratio = 4:1, the mixture was refluxed for 3 h.

Zhao et al. [117] tried to catalyze PC/MeOH transesterification by using KX zeolites. Very low activity of pure KX/NaX was detected, indicating that the basicity of alkali cation-exchanged zeolite is not enough for catalyzing transesterification. Addition of KOH/K$_2$CO$_3$/KNO$_3$/KCl to the KX zeolite improved catalytic activity of the catalyst, but this activity was mainly related to the introduction of known homogeneous alkali metal compounds.

Bhanage et al. [118] found that smectites (one of the layered clay minerals) containing Mg and/or Ni are excellent heterogeneous catalysts for the EC/MeOH transesterification. Both DMC and EG selectivity were very high. Around 75 mol.% of EC conversion and 90 mol.% selectivity to the DMC and EG was achieved. Catalytic performance was dependent upon the amount of alkali metals introduced in the lattice. Reaction conditions: 50 ml stainless autoclave, EC 25 mmol, MeOH 200 mmol, MeOH:EC molar ratio = 8:1, catalyst 0.45g, 150°C, 1MPa of CO$_2$, reaction time 4h. The dependence of catalytic activity of alkali metal load allows supposing that leaching of alkali metal will be a main problem for this catalyst and the catalyst has mainly homogeneous character. Unfortunately no information about reusability of the catalyst is given.
Wei et al. [119] used CaO as a heterogeneous catalyst for PC/MeOH transesterification. Many factors like MeOH:PC ratio, catalyst concentration, temperature, addition method were investigated. It was found that increased catalyst concentration above 0.6 wt.% doesn’t increase PC conversion, but decreases DMC selectivity. Temperature around 30°C was found as optimum. Up to 72 mol.% of PC conversion and 90 mol.% of DMC selectivity was reported. Reaction conditions: MeOH:PC molar ratio = 10:1, 30°C, 0.61 wt.% catalyst concentration. Reaction equilibrium was reached after 30 min reaction time. Reaction mechanism was proposed which can be seen in the next Chapter 2.5.4. Unfortunately, no information about reusability of the CaO catalyst was given. In another work of these authors [120] they mentioned that “ultra fine CaO prepared from CaCO\textsubscript{3} is difficult to filter from the products and reuse”.

So Wei et al. [120] tried to bring CaO on the stable carrier using CaO/carbon composites. Lower activity at room temperature of CaO/C was observed. If temperature was increased to 50°C, reaction equilibrium was reached after around 1h reaction time (around 40 mol.% PC conversion and DMC yield). If particle size 0.18-0.28 mm was chosen, catalyst can be reused at least two times without deactivation. Thereagainst bigger particle size of the catalyst leads to the fast catalyst deactivation (in case of 0.4-0.9 mm – only 10% PC conversion during first reuse). Reaction conditions: MeOH:PC molar ratio=4:1, catalyst load 1.8wt.%, particle size 0.18-0.28 mm, stirring speed 1000 rpm, 323 K (50°C).

Furthermore, Wei et al. [121] published investigations about influence of base strength and basicity of catalyst on catalytic behavior. They proposed that increase of the base strength lead to lower reaction temperature needed. On the other hand very strong base strength can have negative influence on the DMC selectivity due to the promotion of PC polymerization, described in [119]. Increasing of basicity leads to the reducing of induction period and also increases reaction rate. Very small effect of DMC selectivity decrease was observed.

Feng et al. [122] reported about immobilized tertiary amine, which was covalently bonded, to the surface of mesoporous MCM-41 molecular sieve. Strong influence of the reaction temperature, pressure and LHSV was detected. By temperature increase from 110°C to 160°C EC conversion increases from 25 mol.% to 42 mol.%. After 160°C no further EC conversion occurs. Also increase of pressure until 1.0 MPa favors the EC conversion. Pressure more than 1.0 MPa has no positive influence. Thereagainst increase of LHSV has negative effect due to
reduced residence time. Immobilized catalyst exhibited excellent stability and was used for 100h without any obvious loss of activity. Reaction conditions: stainless steel tube reactor, 3.5 g of catalyst, 120°C, 0.2 MPa, MeOH:EC=8:1, LHSV 3h⁻¹.

Jeong et al. [123] investigated quaternary ammonium salts as PC/MeOH transesterification catalyst. They found that conversion of PC increases with the increase of alkyl chain length of the cation. More nucleophilic anion have the same effect. High pressure of CO₂ was favorable for the inhibition of PC decomposition to PO and CO₂ in accordance with [118]. Pseudo-first reaction order was detected and activation energy was calculated as 37.7 kJ/mol. No information about heterogeneous character of the catalyst or its reusability is given. Reaction conditions: steel autoclave, 250-400 psig CO₂ pressure, 140°C, 6h reaction time, MeOH:PC molar ratio = 8:1, catalyst amount 2 mmol.

Y.Chen et al. [124] described PC/MeOH transesterification over ZnO-PbO heterogeneous catalyst. The conversion of PC, selectivity of DMC and yield of DMC reached 63.8%, 97.8%, and 62.4%, respectively. Reusability of catalyst was examined and cause of deactivation was analyzed. Reaction conditions: 110°C, reaction time 2 h, MeOH:PC molar ratio = 8.4, mass fraction of catalyst 3.0%.

Dhuri and Mahajani [125] showed high activity of Amberlyst-21 as heterogeneous catalyst for EC, PC/MeOH transesterification. In case of EC up to 37 mol.% of EC conversion and 95 mol.% DMC selectivity was achieved. For PC: 22 mol.% of PC conversion with 95 mol.% DMC selectivity. Very good reusability of the Amberlyst-21 was shown. No activity or products selectivity loss after 5 reaction cycles were detected. Reaction conditions: slurry reactor, MeOH:EC/PC molar ratio = 8:1, 120°C, catalyst loading 22.488 kg*m⁻³. Amberlyst-21 showed good reusability properties, but its activity was only a half of that of homogeneous catalysts like e.g. NaOH. If 8:1 molar excess of MeOH to PC is used, up to 70 mol.% PC conversion with close to 100% DMC and PG selectivity at room temperature is possible by using of NaOH. Thereagainst Amberlyst-21 achieved only 22 mol.% of PC conversion.

Wang et al. [126] reported about successful use of CaO-ZrO₂ solid solution catalyst. This catalyst was prepared by coprecipitation. XRD, XPS and CO₂-TPD analysis showed that Ca²⁺ ion substituted for Zr⁴⁺ ions in the host lattice and formed homogeneous CaO-ZrO₂ solid solution. When Ca/(Ca+Zr) ratio was 0.1 to 0.3 true solid solution was formed and good
reusability of catalyst was achieved. By using reactive distillation constant PC conversion of around 90 mol.% during 200 h reaction time was shown. In batch reactor around 50 mol.% PC conversion at 440K was achieved. Increase of the CaO loading improves of catalytic performance, but had negative influence on the catalyst stability. In reactive distillation strong drop of PC conversion from 95 mol.% to 70 mol.% after 200 h reaction time was observed when ratio 0.5 Ca/(Ca+Zr) was used. Reaction conditions: stainless batch reactor, 0.5 g of catalyst, 0.2-0.3 mm particle size, MeoH:PC molar ratio = 6:1 (batch reactor), 2 h reaction time. Reactive distillation: 0.71-0.1 mm particle size, 15 g catalyst, LHSV = 0.03 h\(^{-1}\), 423K, 0.5 MPa.

Sankar et al. [127] described successful use of tungstate-based solid catalyst. Around 80 mol.% EC conversion with close to 100 mol.% DMC selectivity was achieved (at room temperature and pressure). Also excellent reusability of Na\(_2\)WO\(_4\)*2H\(_2\)O was shown. No loss of activity during two reactions cycles of recovered catalyst was detected. These results are the best that was published to the time of writing this work.

Also transesterification of PC and MeOH was done by these authors. Only 25 mol.% of PC was converted after 5 h reaction time (23 mol.% DMC yield). If 3.4 MPa CO\(_2\) pressure and 150°C was applied the PC conversion increased to 54 mol.% with 40 mol.% DMC yield. So use of PC instead of EC hinders notably the DMC formation. Reaction conditions: batch reactor, 50 mmol EC, 500 mmol MeOH, MeOH:EC molar ratio = 10:1, 1g of catalyst, CO\(_2\) pressure of 3.4 MPa (if needed), p-xylene – internal standard, 4h reaction time.

### 2.5.4 Proposed reaction mechanism in liquid phase

Reaction mechanism of transesterification of PC and MeOH using CaO was proposed in [119].

Knifton [104] reported that hydroxyethyl methyl carbonate (HEMC), which could be detected only at short reaction time and/or low temperatures, was an intermediate when MeOH reacted with ethylene carbonate, catalyzed by a basic catalyst, to generate DMC and ethylene glycol. Since CaO is a typical solid base, hydroxypropyl methyl carbonate (HPMC) may be the intermediate in the synthesis of DMC from PC and MeOH on CaO. On the basis of this assumption, the charge distributions for MeOH, HPMC and PC were calculated by [119] by use of Guassion 98. Table 6 lists the charge of the oxygen and hydrogen in the hydroxyl group and/or the carbon in the carbonyl group of these three molecules.
Table 6: Charge Distribution of MeOH, HPMC and PC [119]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$O_a$</th>
<th>$H_b$</th>
<th>$C_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>-0.614</td>
<td>0.393</td>
<td>-</td>
</tr>
<tr>
<td>HPMC</td>
<td>-0.620</td>
<td>0.391</td>
<td>0.803</td>
</tr>
<tr>
<td>PC</td>
<td>-</td>
<td>-</td>
<td>0.771</td>
</tr>
</tbody>
</table>

NOTE: Atoms in the molecules are illustrated as follows:

Usually a transesterification reaction catalyzed by a base is taken place when the nucleophilic agent attacks the electrophilic carbonyl carbon of the ester. Thus, when PC transesterifies with MeOH, the oxygen of methanol attacks the carbonyl carbon of PC to initial formation of HPMC (as on Eq. 15-17 shown). HPMC has both nucleophilic hydroxyl oxygen and an electrophilic carbonyl carbon. It cannot only react with MeOH to give DMC but also react with PC to give the polypropylene carbonate (PPC). The two reactions are competitive. From Table 6 it can be seen that the charge on the oxygen in MeOH and HPMC is -0.614 and -0.620, respectively, while the carbonyl carbon in HPMC and PC is 0.803 and 0.771, respectively. It is widely accepted that for nucleophilic substitution reactions, a high electron density for the nucleophilic agent and a high positive charge for the attacked atom are beneficial to decrease the energy of the transition state and subsequently increase the reaction rate [128]. As a result, the free energy for the reaction of HPMC with MeOH is lower than that for MeOH with PC as well as that for HPMC with PC. The reaction rate of HPMC with MeOH is faster than that of MeOH with PC as well as that of HPMC with PC.

In summary, for the synthesis of DMC from PC and MeOH, the intermediate is HPMC, which may be detected only at low temperatures and/or short reaction times. This is because the reaction rate of HPMC with MeOH is much faster than that of PC with MeOH. On the other hand, HPMC can continually react with PC to give the side product, PPC, with a rate much slower than that of the transesterification reaction.
So, this reaction is a nucleophilic substitution reaction. The nucleophilic agent is MeOH and the main function of CaO is to activate MeOH. Iizuka [129] reported that alcohol could be adsorbed on the surface of CaO with $\text{H}^{\delta+}$ being dissociated by surface $\text{O}^{2-}$ and the anion being stabilized by surface $\text{Ca}^{2+}$. Therefore, the mechanism of synthesis of DMC from PC and methanol on CaO is proposed as shown on Eq. 18, 19a and 19b [119].

First, MeOH was activated due to the abstraction of $\text{H}^{\delta+}$ by $\text{O}^{2-}$. Then, $\text{CH}_3\text{O}^{\delta-}$, which is stabilized by $\text{Ca}^{2+}$, reacts with PC to generate $\text{CH}_3\text{OC(O)OCH(CH}_3\text{)}\text{O}^{\delta-}(\text{B}^{\delta-})$ stabilized by $\text{Ca}^{2+}$. Afterwards, $\text{CH}_3\text{O}^{\delta-}$ stabilized in the neighborhood of $\text{B}^{\delta-}$ would react with $\text{B}^{\delta-}$ to give both DMC and $\text{O}^{\delta-}\text{CH}_3\text{CH}_2\text{CH}_3\text{O}^{\delta-}(\text{C}_2^{\delta-})$ stabilized by two consecutive sites. Finally $\text{C}^{\delta-}$ abstracts two neighbors $\text{H}^{\delta-}$ from $\text{O}^{2+}$ to form propylene glycol and desorbs from surface of CaO.
Many catalytic systems have been reported for the transesterification of cyclic carbonates and methanol. Its differentiation into the homogeneous and heterogeneous systems is often very difficult due to the several reasons. That can be dispersion of the catalyst particles in liquid phase reactions like it is the case with CaO [120]. Next reason can be intensive leaching of the active homogeneous components from the carrier (e.g. leaching of KOH from KX catalyst [117]). Also absent information of the stability and reusability makes the estimation of the catalytic system heterogeneity difficult.

Homogeneous catalysts showed good activity even at room temperature and pressure (up to 70 mol.% conversion and yield) but its industrial application is hindered due to the problems of catalyst separation after reaction and reusability.
Nevertheless some catalytic systems have without any doubts heterogeneous nature (e.g. [125, 126, 127]). Most of the heterogeneous catalytic systems need severe reaction conditions (i.e. high pressures up to 3 MPa and temperatures in range of 110-250°C) to obtain even moderate DMC yield (mostly around 40 mol.% conversion at 80 mol.% selectivity). The best results were published in [127], were high EC conversion at room temperature and pressure was reported (80 mol.% EC conversion and DMC yield), during PC conversion remain very low (25 mol.%).
3 Results and Discussion

3.1 Ethyl benzene to styrene

3.1.1 Introduction

Process of co-producing of styrene, ethane and hydrogen as in Eq. 4 shown, was successful developed and implemented by Dow Chemical Co. They have been running a pilot plant scale unit in Houston, using a circulating fluidized bed reactor with catalyst residence times of several minutes. However, Dow expects the activity of the catalyst to be significantly higher during its first seconds of Time On Stream (TOS) compared the activity after several minutes TOS due to the catalyst deactivation. This would imply the use of a riser reactor instead of fluidized bed unit to obtain the required catalyst residence times.

In order to investigate this problem a co-operation between the department of Chemical Technology and Heterogeneous Catalysis of the RWTH Aachen University, Prof. Wolfgang Hölderich, was established. In this project a laboratory scale riser reactor was to be conceived, in which residence times in the order of magnitude of seconds were envisaged. After performing these tasks (vide infra), another important questions appeared which solution was also performed and is presented in this work. Different problems regarding influence of the different factors like temperature, carbon dioxide and water addition to the feed as well as looking for the possible oxygen source due to the strong CO2 formation during running of pilot plant were investigated.

The reactions were performed in the riser-reactor, which set up, as well as picture without isolation and cooling trap are shown in the Figure 17 and Figure 18. For reactor details and reaction procedure please refer to the Chapter 5 - Experimental.
Figure 17: Riser-reactor set up
3.1.2 Definitions and flow calculations

Gas Residence Time (GRT) in the riser reactor was defined as follows:

$$\text{GRT} = \frac{\text{Reactor volume (m}^3\text{)}}{\text{Total gas flow at reaction temperature (m}^3\text{)}}$$  \hspace{1cm} (20)
Results and Discussion – Ethyl Benzene to Styrene

Also calculations to estimate solid catalyst consumption were performed. The calculations were performed for intermediate gas flow regime (0.1<Re<1000). As it can be seen in Table 7 at longer GRT’s calculated solid flow corresponds better with the experimental data.

<table>
<thead>
<tr>
<th>Internal experiment name</th>
<th>GRT (s)</th>
<th>Superficial gas velocity (m/s)</th>
<th>Solids flow theoretical (kg/h)</th>
<th>Solids flow experimental (kg/h)</th>
<th>Gas flow (l/h)</th>
<th>Cat/Gas theoretical (wt/wt)</th>
<th>Cat/Gas experimental (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMDOW9</td>
<td>0.78</td>
<td>0.64</td>
<td>10.2</td>
<td>14</td>
<td>45.31</td>
<td>392</td>
<td>542</td>
</tr>
<tr>
<td>DMDOW7</td>
<td>0.7</td>
<td>0.71</td>
<td>12</td>
<td>24.13</td>
<td>50.5</td>
<td>416</td>
<td>838</td>
</tr>
</tbody>
</table>

The terminal velocity of a single particle \( U_t \) was calculated as in [130] described:

\[
U_t = \left[ \frac{4 \cdot g \cdot d_p \cdot (\rho_p - \rho_g)}{3 \cdot \rho_g \cdot C_D} \right]^{1/2} \tag{21}
\]

where

\( d_p \) = particle diameter,

\( \rho_p \) = particle density,

\( \rho_g \) = gas density at reaction temperature (ASPen data).

\( C_D \) was calculated as follows [130]:

\[
C_D = \left( \frac{24}{R_e_p} \right)^* \left( 1 + 0.14 \cdot R_e_p^{0.7} \right) \tag{22}
\]

\[
R_e_p = \frac{U_t \cdot d_p \cdot \rho_f}{\mu_g} \tag{23}
\]

where

\( U_t \) = terminal velocity of a single particle,

\( d_p \) = particle diameter,

\( \rho_g \) = gas density at reaction temperature,

\( \mu_g \) = gas viscosity at reaction temperature.
After calculations of $U_T$ hindered setting corrections for the high particle concentration were performed as in [131] and [132] described:

\[ U_t = U_{t0} * (1 - c)^n \]

, where

$U_t$ = terminal setting velocity,
$U_{t0}$ = terminal velocity of a single sphere (infinity dilution),
c = volume fraction solid in the suspension,
n = function of Reynolds number $Re_p$ (n=4.3).

Also the models for Stoke’s and Newton’s laws ($Re<0.1$ and $Re>1000$) were tried to perform the calculations, but the obtained values were even more outside the experimental data. The deviations are possibly conditioned by non-spherical particles form as well non-ideal gas behavior at high temperatures.

### 3.1.3 Reaction conditions and products

The reaction of EB and ethane were performed at 600°C (873 K) reactor temperature. A typical product mixture consists of unconverted EB, styrene and a small amount of benzene. In addition toluene, naphthalene, biphenyl and other components, which are described below as “others” were found in more or less negligible amounts. The gaseous product mixture contains ethane, ethene, methane and carbon dioxide. Thermogravimetric analysis of spent catalyst didn’t show present of any deposits on catalyst particles.

Before performing experiments with co-feeding of ethane to EB, experiment only with EB as a feed was performed to detect the necessary of ethane adding to the feed. The reaction conditions are 600°C (873 K), 0.68 s GRT and nitrogen as carrier gas. Around 27 mol.% of styrene could be detected in liquid product mixture, 2.2 mol.% of benzene and 2.7 mol.% of “others”. The rest was unconverted EB. A lot of carbon dioxide was found in gaseous mixture - around 90%, followed by methane with 8% as well as ethane and ethene as rest. The styrene yield was only 7 mol.%.
3.1.4 **Influence of Gas Residence Time (GRT)**

Effect of GRT was investigated at 20 and 40 mol.% of ethyl benzene in the feed. Figure 19 represents the product distribution in case of 20 mol.% of EB. As it can be seen the styrene concentration increases significantly by increasing the GRT, on contrary the EB concentration drops. At 1 s GRT around 56 mol.% of styrene and only 32 mol.% of EB were found as liquid products. The formation of side products like benzene and many other components become significant at longer GRT (after approx. 0.7 s GRT). At 1s GRT around 3.5 mol.% of benzene and 5 mol.% of “others” have been formed (see Figure 19).

The distribution of gaseous reaction products is illustrated on Figure 20. Apart from large amounts of carbon dioxide small amounts of methane and ethane were detected. Formation of CO$_2$ becomes extremely at longer GRT’s. At 1 s GRT more CO$_2$ was detected than ethane. The source of oxygen for oxidation reactions was unclear, so additional experiments for its detection were performed (vide infra).

![Graph showing liquid products distribution](image_url)

**Figure 19:** Liquid products distribution. 20 mol.% of EB, 600°C.
Similar tendencies were observed in the case of 40 mol.% of EB in the feed as shown in Figure 21. However, lower conversion of EB to styrene was found. At 1 s GRT only around 40 mol.% of styrene were detected in the liquid reaction mixture. In contrast to the experiments with 20 mol.% of EB there was only relative low formation of side products. At 1 s GRT only 4 mol.% total side products were detected against 11 mol.% in case of 20 mol.% EB feed.

Figure 22 represents liquid side products formation as a function of styrene formation. As “side products” here are represented all liquid products apart from styrene (i.e. toluene, benzene, naphthalene, biphenyl and “others”). As it can be seen the level of side products formation is relatively constant at the different EB concentrations in the feed at same styrene formation levels. It is a sign that no significant thermal destruction of EB and/or other hydrocarbons occurs during this reaction. Otherwise strong increase of side products formation at longer GRT’s and higher EB content in the feed were to expect. So it can be assumed that the side products formation is a function of EB conversion (and styrene formation).
Results and Discussion – Ethyl Benzene to Styrene

Figure 21: Liquid products distribution. 40 mol.% of EB, 600°C.

Figure 22: Liquid side products formation at different styrene formation levels, 600°C.
3.1.5 Influence of ethyl benzene content in the feed

The Figure 23 represents the concentration of styrene, unconverted EB and “others” in the liquid reaction mixture using different EB concentrations in the feed. The formation of desired styrene decreases slightly by increasing amount of EB in the feed. The concentration of unconverted EB grows in mixture. A constantly low side products formation was observed.

![Figure 23: Influence of the EB concentration in the feed, 0.68 s GRT and 600°C.](image)

3.1.6 Oxygen in the reaction

In order to detect the source for the high amount of carbon dioxide in the gaseous product various “blank” experiments using only nitrogen as a feed were performed. Around 3% of oxygen was found in the product mixture after the blank test. It can be assumed that in the catalyst pores contained oxygen is a source for that. Also flushing the catalyst with argon during 30 min at fluidized conditions before reaction resulted in the same oxygen content as in the blank reaction. It seems that oxygen adsorbed in catalysts pores cannot be effectively removed by flushing and is responsible for oxidation reactions and high carbon dioxide content in gas products.
3.1.7 Temperature influence

Other experiments were performed in order to detect the influence of oxygen always present yielding carbon dioxide. Experiments using only ethane as feed were carried out at 600°C and 700°C in the presence of catalyst, at 0.7 s GRT. Figure 24 represents the results. As it can be seen a lot of CO₂, 8 and 11 mol.%, respectively, were formed at 600 and 700°C. It is logical that all of CO₂ was formed by oxidation of ethane feed. Also a considerable amount of ethene was formed at 700°C, which content was almost equal to the ethane after reaction at 0.7 s GRT.

![Figure 24: Gas products distribution at 600 and 700°C, 0.7 s GRT, only ethane as a feed](image)

3.1.8 Influence of CO₂ in the feed

In order to detect possible influence of additional small amounts of carbon dioxide in the feed on the CO₂ formation some experiments were performed. No significant changes in the CO₂ and other products formation were observed when ethane feed contained 500 ppm of CO₂ at
600°C. Reaction conditions: 0.7 s GRT, 600°C. No changes in methane or ethene formation were detected. So at 600°C no influence of CO$_2$ in the feed was detected. Thereagainst at 700°C considerably amount of additional carbon dioxide, around 3% (13.4% versus 10.6%), more CO$_2$ were produced.

### 3.1.9 Gas Residence Time influence

The effect of GRT on the amount of carbon dioxide produced during the reaction of EB and ethane is illustrated in Figure 25. CO$_2$ formation grows exponential by increasing GRT. Already at 1 s GRT a half of the gaseous products consist from carbon dioxide. Figure 26 represents the product distribution at 0.7 and 1 s GRT only with ethane as a feed at 700°C. A similar tendency to increased carbon dioxide production at longer GRT can be observed. Also a strong increase of methane production was detected opposite to the experiments with EB in the feed (see Figure 25).

![Figure 25: Gaseous product distribution. 20 mol.% of EB, 600°C](image-url)
Figure 26: Gas product distribution at 0.7 and 1 s GRT. 700°C, only ethane as a feed

3.1.10 Water influence

30 mol.% of water were added to the ethane feed to investigate its possible influence. Reaction conditions are only ethane as a feed, 700°C and 1s GRT. As demonstrated in Figure 27 a considerable reduction of methane and CO₂ formation can be observed. Also small increase of ethene formation was detected.

The partial pressure of the ethane was reduced in this experiment compared to that in the experiment only with ethane in the feed. Possibly it was the reason for the lower CO₂ and methane content in the product mixture. So experiments with the same ethane concentration (i.e. same ethane partial pressure) as in presence of water were performed (“blank” experiment). This “blank” experiment allowed to test if these changes in carbon dioxide and methane production are caused by water presence. Table 8 represents comparison of the feed gases of these two experiments. As it can be seen same amount of ethane (42.6 vol.%) was used for both reactions.
Table 8: Feed comparison of water and “blank” experiments

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Water experiment</th>
<th>“Blank” experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow in Nl/h</td>
<td>Flow at 700°C in l/h</td>
</tr>
<tr>
<td>Ethane</td>
<td>6,4</td>
<td>21,3</td>
</tr>
<tr>
<td>Water</td>
<td>3,0</td>
<td>9,9</td>
</tr>
<tr>
<td>Nitrogen (anti-arching)</td>
<td>5,7</td>
<td>18,9</td>
</tr>
<tr>
<td>Total</td>
<td>15,1</td>
<td>50,1</td>
</tr>
</tbody>
</table>

Figure 28 represents an experiment with 30 mol.% of water in ethane feed and “blank” experiment with 30 % of nitrogen and ethane (it should be mentioned that also additional nitrogen as “anti-arching” flow was used in every experiment – see Chapter 5 Experimental). Up to 2.5 times more CO$_2$ (32% vs. 12%) was formed when nitrogen was used instead of water. Thus, the water presence prevents the oxidation of ethane. Also destruction of ethane to methane is hindered.

![Figure 27: Gas products distribution with and without water adding. 1 s GRT, 700°C.](image-url)
3.1.11 Conclusions and Outlook

Influence of the different factors on the formation of carbon dioxide and other products were studied in the reaction of ethyl benzene with ethane in a riser reactor.

The increase of EB concentration in the feed from 20 mol.% to 40 mol.% leads to some decrease of the styrene formation.

Gas residence time is one of the main reaction parameters in the riser reactor. Longer GRT increases the styrene yield but also leads to the stronger side product formation, such as carbon dioxide and methane. The amount of the side products directly dependent upon the styrene formed.

Using only ethane as feed, high temperatures and long GRT’s lead to an increase of methane and carbon dioxide formation.

Figure 28: Water experiment and blank experiment. 1 s GRT, 700°C.
The possible source of oxygen in the reaction is the catalyst itself. Oxygen in the catalysts pores causes the oxidation of ethane and/or of EB to CO$_2$. Use of only nitrogen as a feed in a blank experiment as well as argon flushing the catalyst prior to the experiments didn’t lead to the reduction of the oxygen content in the product mixture.

The influence of carbon dioxide present in the feed was studied. 500 ppm CO$_2$ in the feed has an influence on CO$_2$ formation only at 700°C. No differences at 600°C could be detected.

Positive effect to reduce the side products formation by addition of water to the feed was observed. A 30% less CO$_2$ was formed at 1 s GRT and 700°C if 30 mol.% water was added to the feed.

It is recommended to run the reaction under following conditions in the riser reactor:
EB concentration range 20-30 mol.%, GRT range 0.8-1.0 s, water concentration range 10-30 mol.%.
3.2 Methane Dehydroaromatization over Mo/HZSM-5

3.3.1 Overview and Definitions

A fixed bed and fluidized bed reactors were used for the experiments performing. Flow sheet diagram of the fixed bed reactor can be seen in Figure 28. Fluidized bed reactor P&I diagram and set up are presented in Figure 30 and Figure 31. For more information please refer to the Experimental part.

![Flow sheet diagram of the MDA fixed bed reactor system](image1.png)

Figure 29: Flow sheet diagram of the MDA fixed bed reactor system

![P&I diagram of the fluidized bed reactor system](image2.png)

Figure 30: P&I diagram of the fluidized bed reactor system
Definitions of methane conversion, aromatic formation rate, yield and selectivity are given in the Equations 25-28:

Aromatic formation rate (mmol “C”/g cat * h) = \frac{\text{carbon in aromatics formed (mmol)}}{\text{catalyst load (g) * TOS (h)}} \quad (25)

Conversion (mol%) = \frac{\text{mol CH}_4\text{fed} - \text{mol CH}_4\text{out}}{\text{mol CH}_4\text{fed}} \quad (26)

Yield (mol%) = \frac{\text{Amount of aromatic formed (mol) * No. carbon atoms within aromatic}}{\text{mol CH}_4\text{fed}} \quad (27)

Selectivity (mol%) = \frac{\text{Amount of Aromatics formed (mol)}}{\text{mol CH}_4\text{fed} - \text{mol CH}_4\text{out}} \quad (28)
3.3.2 Fixed-bed reactor results

The Figure 32 and Figure 33 show the typical aromatic formation rate and distribution during the reaction at 973K when only methane was used as feed. WHSV was maintained at a rate of 2.0 g CH$_4$ / g cat*h.

The formation rate of the aromatic products increases very rapidly during the first 40 minutes and arrives a maximum. And after that it decreases slowly because of the coke deposits on the catalyst particles - see Figure 32. As it can be seen, this reaction is very selective to the benzene formation. At the start of the reaction benzene content is around 84% of all the aromatics formed. The longer TOS the lower is the naphthalene production and the higher is the selectivity to benzene, which grows up to 95% of total aromatics formed (see. Figure 33) after 470 min TOS. Toluene formation is almost constant and consist 1-2 mol% during all reaction times (Figure 33).

Figure 35 shows the course of the catalyst’s activity during 16 reaction cycles. A maximum of the yield of around 7 mol.% aromatics can be achieved. A long-term deactivation occurs after 11 cycles (that corresponds to 55 h in total TOS). The catalyst after 16 reaction cycles was undergone XRD, ICP-AES, BET and TGA analysis in order to detect changes in the catalyst’s structure and properties.

The XRD analysis of the fresh catalyst and the spent catalyst after 16 reaction cycles is shown below in Figure 35. Three analyses were performed for each sample, and figures of intensity were averaged over the 2$\theta$ scale.

The diffraction patterns of the spent catalyst were not as intense as those of the fresh, starting material. The intensity of the diffraction at ca. 23°, decreased respectively from 187 cps to 156 cps after 16 reaction cycles. Assuming a crystallinity of 100% for the fresh catalyst, the spent catalyst suffered a loss of crystallinity of around 16%. This might be caused by a partial destruction of the lattice, caused by repeated heating of the catalyst to the reaction temperature of 700°C. There was no secondary phase formation observed.
Figure 32: Aromatic formation rate. 973K, WHSV=2.0 h\(^{-1}\), fixed-bed reactor

Figure 33: Aromatic distribution. 973K, WHSV=2.0 h\(^{-1}\), fixed-bed reactor
Figure 34: Yield of the aromatic in mol.% and its distribution during 16 reaction cycles. 973K, fixed bed reactor

Figure 35: X-Ray diffraction of the fresh Mo/HZSM-5 and the spent catalyst after having undergone 16 reaction cycles
Table 9 represents the surface area, measured by BET method. A decrease of the nitrogen sorption capacity of the catalyst after 16 reaction cycles was observed. However, this decrease was minor (see Table 9). The BET surface area decreased from 288 to 276 $m^2/g$, the micropore surface area from 189 to 184 $m^2/g$, and the micropore volume decreased from 0.092 to 0.090 $cm^3/g$. Such decreases may be attributed to a somewhat loss in crystallinity, as previously shown, which would have caused a partial collapse of the structure. However, such a loss was only minor and appeared to be of no significance.

Elementary analysis of the substances revealed no recognizable trend in the aluminum, silicon or molybdenum transfer (see Table 10). Such small deviations in the above calculated ratios cannot be interpreted, as they clearly lie within the error of measurement of the techniques involved. The other consideration is that within gas phase reactions, leaching of elements is rather unlikely (at the given temperatures).

TGA analysis was applied to the coked catalyst. Figure 36 represents the typical TGA and DTG curves. The first mass loss process (Peak 1) occurs at 688K (415°C). According to the references [75] and [77], this mass loss process can be attributed to the coke formed on the Mo$_{x}$O$_{y}$-species. The second peak (Peak 2 - 465°C/738K) can be attributed to the coke formed on the free Brönsted acid sites of HZSM-5. There is no described in [77] third mass loss process was detected which can be ascribed to the coke, formed on the Mo-species not associated with Brönsted acid sites. According to [75] all of MoO$_{x}$ species were associated to the Brönsted acid sites during long activation/regeneration period of 18h. This is the reason for the absence of the third mass loss process on TGA analysis data.
Figure 36: TGA analysis of used catalyst. Mass loss, DSC and DTG, air, 2K/min

Table 9: Summary of nitrogen sorption and BET surface area analyses for the fresh Mo/HZSM-5 and for the spent catalyst after having undergone 16 reaction cycles.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²/g)</th>
<th>Micropore Surface Area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>288</td>
<td>189</td>
<td>0.092</td>
</tr>
<tr>
<td>Used catalyst</td>
<td>276</td>
<td>184</td>
<td>0.090</td>
</tr>
<tr>
<td>Loss in %</td>
<td>4.2</td>
<td>2.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 10: Summary of ICP AES analyses for the fresh Mo/HZSM-5 and for the spent catalyst after having undergone 16 reaction cycles.

<table>
<thead>
<tr>
<th></th>
<th>Si/Al (mol/mol)</th>
<th>Si/Mo (mol/mol)</th>
<th>Al/Mo (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>16.3</td>
<td>29.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Used catalyst</td>
<td>15.0</td>
<td>32.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>
3.3.3 Fluidized bed reactor results

3.3.3.1 Yield and selectivity

The reactions were performed at 973K and WHSV of 1.4 g CH₄/g Cat*h (this corresponds to the VHSV level of 2000 ml CH₄/(g cat*h)). Fluid dynamic investigations were performed prior to the use of every catalyst batch and Minimal Fluidization Velocity (MFV) was calculated. For more information see Chapter 5.1.3.

As it can be seen on the Figure 37 and Figure 38 Mo/HZSM-5 is very active as a catalyst in the first reaction run. Methane conversion reaches 8 mol.% and depletion rate of methane reaches 6.3 mmol C/g Cat*h. After that a strong long-term deactivation of the catalyst occurs. During the second and the third run depletion rate values of only 1.8 and 1.4 mmol C/gCat*h respectively can be observed (Figure 38).

Figure 39 represents the aromatic distribution during first reaction run in the fluidized bed reactor. Stronger naphthalene formation can be realized at the maximum point of the aromatic formation. Selectivity to the benzene has a minimum at the point of the maximum catalytic activity. Production of toluene is relative constant during the total reaction time. After the maximum of aromatic formation the naphthalene selectivity drops to a similar values as in the fixed bed reactor of around 4-7 mol.% with a decreasing trend (Figure 39).

Figure 40 represents the aromatic distribution in the third reaction run. The selectivity to benzene maintains at a very high level of more than 95% during entire reaction time. A formation of a higher amount of naphthalene at the reaction start can be observed but is not as clear as in the first reaction cycle. The reason for it is general catalyst deactivation which results in the total activity drop (see next Chapter 3.3.3.2).
Figure 37: Methane conversion in fluidized bed reactor. Three reaction cycles are shown. 973K, WHSV=1.44 h⁻¹

Figure 38: Aromatic formation rate in mmol “C”/g*h for fluidized bed reactor. Three reaction cycles are shown. 973K, WHSV=1.44 h⁻¹
Figure 39: Aromatic distribution in mol.% for fluidized bed reactor. First reaction cycle is shown, 973K.

Figure 40: Aromatic distribution in fluidized bed reactor. Third reaction cycle is shown, 973K.
3.3.3.2 Catalyst analysis

In order to detect some changes in the catalyst structure after three reaction cycles in the fluidized bed reactor the catalyst was investigated by BET, ICP-AES and XRD analysis. Total reaction time during 3 reaction cycles in the fluidized bed (reaction conditions: methane WHSV 1.4 h\(^{-1}\), 700°C (973 K)) was 20 hours and common activation and regeneration time (conditions: WHSV=1.4 h\(^{-1}\), 580°C (853 K)) was 72 hours.

It is illustrated in Table 11 that the catalyst lost around 41% of its BET surface, and about 45% of its micropore surface area and volume. Such significant loss of active micropores has a heavy effect on the catalyst performance (vide infra).

Table 12 shows results of ICP-AES analysis. A decrease of Si/Al ratio from 16.3 to 13.1 was detected. In addition a significant loss of Mo loading was observed. In case of the used catalyst the Al/Mo ratio increased from 1.8 to 2.3. It seems that the intensification of the Mo-leaching occurs under fluidized conditions, compared to the fixed bed reaction at same reaction conditions.

XRD-analysis was performed for spent catalyst. A significant loss of the intensities of the diffraction patterns at different 2-Theta degrees was detected. This is a sign of crystallinity loss. Table 13 represents the results of XRD-analysis. Up to 34% of crystallinity loss could be detected. The repeated heating up and cooling down of the catalyst might be a reason for it. Also mechanical attrition of the particles could be possibly the reason for decreasing of crystallinity and surface area (see also next Chapter 3.3.3.3).

All these changes in the catalyst structure under fluidized conditions resulted in the significant activity loss of the catalyst already after 4h TOS at 700°C and at 1.44 h\(^{-1}\) methane WHSV as in Figure 38 presented (with one regeneration cycle of 20 h at fluidized conditions between). Also significant changes in the formed aromatic distribution can be detected, see Figure 40. High benzene selectivity (more than 95 mol.%) and relative high toluene formation at longer TOS were observed. In contrast to this amount of naphthalene formed was less than in the case of fresh catalyst. It can be assumed that the methane residence time on catalyst particles decreased significantly in case of used catalyst. Less micropores in the catalyst structure lead to the limited aromatic formation and to the prevailed formation of benzene and/or toluene.
No conditions for the formation of sequent to the benzene products like naphthalene are present after destruction of catalysts micropores.

Table 11: Summary of nitrogen sorption and BET surface area analyses for the fresh Mo/HZSM-5 and for the spent catalyst after having undergone 3 reaction cycles in fluidized bed reactor

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>288</td>
<td>189</td>
<td>0.092</td>
</tr>
<tr>
<td>Used catalyst</td>
<td>170</td>
<td>104</td>
<td>0.051</td>
</tr>
<tr>
<td>Loss in %</td>
<td>41</td>
<td>45</td>
<td>44.5</td>
</tr>
</tbody>
</table>

Table 12: Summary of ICP AES analyses for the fresh Mo/HZSM-5 and for the spent catalyst after having undergone 3 reaction cycles in fluidized bed reactor

<table>
<thead>
<tr>
<th></th>
<th>Si/Al (mol/mol)</th>
<th>Si/Mo (mol/mol)</th>
<th>Al/Mo (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>16.3</td>
<td>29.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Used catalyst</td>
<td>13.1</td>
<td>29.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 13: Changes in X-Ray diffraction for the fresh Mo/HZSM-5 and for the spent catalyst after having undergone 3 reaction cycles in fluidized bed reactor

<table>
<thead>
<tr>
<th>2-Theta</th>
<th>Fresh catalyst</th>
<th>Used catalyst</th>
<th>Loss in %</th>
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<tbody>
<tr>
<td>7.90</td>
<td>341</td>
<td>288</td>
<td>15.5</td>
</tr>
<tr>
<td>8.78</td>
<td>208</td>
<td>161</td>
<td>22.6</td>
</tr>
<tr>
<td>23.04</td>
<td>502</td>
<td>365</td>
<td>27.3</td>
</tr>
<tr>
<td>23.86</td>
<td>295</td>
<td>194</td>
<td>34.2</td>
</tr>
<tr>
<td>45.32</td>
<td>117</td>
<td>93</td>
<td>20.5</td>
</tr>
<tr>
<td>7.90</td>
<td>341</td>
<td>288</td>
<td>15.5</td>
</tr>
</tbody>
</table>

3.3.3.3 Mechanical stability of Mo/HZSM-5 catalyst in the fluidized-bed reactor.

A strong fines blowing out (carry-over) of the catalyst particles was detected in the fluidized bed experiments. In order to investigate the attrition of the catalyst particles, the particle size
distribution analysis was done. During 3 reaction cycles the total reaction time was 20 hours and regeneration time was around 72 hours, so total time under fluidized conditions was about 92 hours. Figure 41 represents the particles size distribution after 3 reaction cycles in the fluidized bed reactor and the fresh catalyst particles size. Initial particles size (depicted in dark color) was 160-400 µm. The light grey columns on the Figure 41 correspond to the particles of the used catalyst. They consist from the initial sized particles and particles, appeared due to catalyst attrition. It can be seen that only around 55% of the initial catalyst particles kept their particles size in the primary range. And from the rest - 26% and 9% are still in the range of 1 µm – 0.16 µm. That is less than initial size but it can be assumed, that they are still participate in the reaction without significant blowing out from the reactor. Around 10% of used catalyst particles have size less than 1 µm after 92 h TOS.

For the use of this catalyst in the fluidized bed reactor its mechanical stability has to be improved.

Figure 41: Particles size distribution of used catalyst after 92 hours under fluidized conditions and fresh catalyst particles.
3.3.4 Comparison of MDA procedure in fixed and fluidized bed reactors

3.3.4.1 Yield and selectivity

Figure 42 represents the formation rate of aromatic for fixed and fluidized bed reactions. The reaction conditions are : 700°C (973 K), methane WHSV=1.4 h\(^{-1}\) or VHSV=2000 ml\(_{CH_4}/g\) \(Cat\)*h. Around 15 % higher conversion rates of methane to aromatic can be reached at the maximum point (after around 60 min TOS) in the fluidized bed reactor – 6.3 mmol C/g\(_{Cat}\)*h against 5.5 mmol C/g\(_{Cat}\)*h in fixed bed. After achieving the maximum point in fluidized bed a strong activity drop was detected. Afterwards the activity level remained at 4.0 mmol C/g\(_{Cat}\)*h and dropped again after 300 min to the level of 2.0 mmol C/g\(_{Cat}\)*h. In contrast to this, the aromatic formation rate in fixed bed reactor was relative constant and decreased from 5.5 to 5.0 mmol C/g\(_{Cat}\)*h during 4h TOS.

This increase of aromatic formation in fluidized bed reactor goes along with some higher level of the naphthalene formation (Figure 38, Figure 39). In contrast to the aromatic distribution in the fixed bed reactor (Figure 33), in case of fluidized bed some more naphthalene formation was detected (despite the reaction start point - Figure 38). Also different behavior at lower reaction temperatures in fluidized bed reactor was observed. At the start of reaction time (i.e. from 580 to 700°C) 91 mol.% of benzene was formed in fluidized bed.

The increased naphthalene formation in the fluidized bed might have its reason in a process of catalyst back mixing. Therefore the total contact time can be longer than in case of fixed bed. The longer contact times lead to the formation of consecutive products such as naphthalene.

Strong catalyst particles destruction in the fluidized bed (vide infra) leads consequently to the destruction of the pores and reducing of the total active species amount. The reasons for it can be e.g. catalyst attrition, heating and cooling process, Mo-leaching. Together with the process of coke formation this results in the stronger catalyst deactivation in the fluidized bed reactor compared to the fixed bed reactor.
3.3.4.2 Comparison of the used catalyst from fluidized and fixed bed reactors

The comparison of the used catalysts in the fluidized and fixed bed reactor respectively will be discussed. The applied reaction conditions in the fixed bed are: reaction time during 16 cycles - 50 hours at 700°C (973 K), activation and regeneration - 200 hours at 580°C (853 K). The conditions in the fluidized bed: reaction time during 3 cycles - 20 hours at 700°C, activation and regeneration - 70 hours at 580°C.

As it can be seen on Tables 1-5, the catalyst used under fluidized bed conditions shows stronger changes in the structure and properties than after use in the fixed bed even after longer TOS. Loss of the BET surface was 41 % versus only 4.2 % in case of fixed bed. About 20-25% loss of crystallinity of the catalyst after use in the fluidized bed reactor was detected. Also some loss of Mo was detected after use in fluidized bed reactor. The reason for these changes can be strong reduction of particles size (Chapter 3.3.3.3) might be a reason for BET and crystallinity loss.
As it can be seen, Mo/HZSM-5 catalyst undergoes strong structural modifications under fluidized conditions.

TGA profiles of both used catalysts showed almost same temperatures of the first mass loss process. Peak 1 was detected at 420°C (688K) for fixed bed and at 415°C for fluidized bed reactor. This coke can be attributed to the coke formed on the MoC$_x$O$_y$-species - [75] and [77]. Peak 2 for catalyst used in the in fluidized bed reactor was shifted towards higher temperature for 20°C (from 438°C for catalyst used in fixed bed to 458°C). This coke can be attributed to the coke formed on the free Brönsted acid sites of HZSM-5 catalyst. More intensive aromatic formation rate in fluidized bed reactor favors intensive HZSM-5 support participating in the catalysis process, causing more intensive coke depositions in it. Total amount of coke on the used catalyst was also higher after use in fluidized bed (4.6 wt.% vs. 3.6 wt.% in fixed bed). Reaction conditions: 700°C, 5h TOS, WHSV=1.44 g$^{-1}$. Third mass loss process described in [77] was not detected. This mass loss can be attributed to the coke, formed on the Mo-species not associated with Brönsted acid sites.

![Figure 43: TGA coke analysis after use in fixed and fluidized bed reactors.](image-url)
3.3.5 Influence of the WHSV on catalytic performance

The variation of the WHSV was investigated. Figure 44 represents the formation rate of the aromatic at different WHSV levels. As it can be seen the maximum of aromatic formation rate grows continuously during increase of WHSV from 0.3 h\(^{-1}\) to 4.3 h\(^{-1}\). Up to 11.5 mmol carbon per g catalyst per hour was formed. However, the deactivation of catalyst becomes very rapid after around WHSV 2 h\(^{-1}\). The reason is a significant coke formation (vide infra).

The methane conversion is relative constant over almost all tested WHSV levels (Figure 45). Starting from WHSV of around 2 h\(^{-1}\), conversion drop after arriving of maximum point was detected. This tendency is more intensive at highest WHSV level of 4.3 h\(^{-1}\).

It seems that the optimal WHSV level lies in the range of 1.4 – 2.0 h\(^{-1}\) (VHSV approx. 2000 – 2800 ml CH\(_4\)/g Cat* h) at which the aromatic formation rate is high and no strong deactivation occurs. The reason why many researcher selected VHSV level of 1500 ml CH\(_4\)/g Cat*h as usual reaction conditions was probably another reactor set up - lower amount of catalyst in the bed and relative big diameter of reactor (i.e. small length/diameter ratio). That has strong influence on the possibility of catalysts particles to contact with methane and lower VHSV optimum is a logical consequence.

As mentioned before, TGA analysis of the formed coke showed two main mass losses. First one occurs at approx. 425°C (698 K) and the second one at ca. 460°C (773 K). Figure 46 represents the temperatures of these two mass loss processes (represented as Peak 1 and Peak 2 respectively), total mass loss in wt.% (on secondary scale) as well as P1 to P2 ratio (on secondary scale), which is ratio of Peak1 area to Peak 2 area. As it can be seen, the temperature required to burn out the coke formed at MoC\(_x\)O\(_y\)-species (Peak 1) goes slowly down or remains constant by increasing of WHSV level. In contrast to this coke formed on the free Brönsted acid sites of HZSM-5 (Peak 2) moderately increases required burn out temperatures at higher WHSV levels (from 445°C at 0.3 h\(^{-1}\) to 480°C at 4 h\(^{-1}\) - Figure 46). This can be a sign for stronger coke formation on the free acid sites at the higher WHSV levels. In order to verify this hypothesis an estimation of the DSC curve area of both mass loss processes was done. The area was determined graphically as a peak height multiplied by peak breadth (at a half of the peak height) on the DSC curve of coke TGA analysis. The ratio of the area of Peak 1 to Peak 2 at the different WHSV levels is represented on Figure 46. It
can be seen that P1/P2 ratio grows significantly by increasing of methane WHSV from 0.4 to 1.0 h\(^{-1}\) (grow from 1.2 to 2.2, respectively). Further WHSV increase from 1 to 4 h\(^{-1}\) leads to the slow P1/P2 increase from 2.2 to 2.36. These observations show that coke formation on the free acid sites becomes more significant at higher WHSV levels. It can be assumed that coke formation increase by WHSV increasing is conditioned by its formation on free acid sites until WHSV level of around 1.0 h\(^{-1}\). During further WHSV increasing coke is formed proportionally on the free acid sites and on the MoC\(_x\)O\(_y\) active species. This seems to be an important reason for the stronger catalyst deactivation at higher WHSV levels. Further catalyst improvement should go in the direction of the reduction of the free acid sites amount up to the minimum which is required for effective trimerization/aromatization of the intermediate C\(_2\)-species what should improve the catalyst service time.

A continuously strong increase of total coke amount was detected. At WHSV of 0.3 h\(^{-1}\) only 3.2 wt.% of coke was formed. At WHSV of 4.3 h\(^{-1}\) three times more coke was formed - 9.8 wt.%.

The strong coke formation remains as main reason for the catalyst deactivation and hence hindrance for the MDA industrial application so far.
Figure 44: Formation rate of aromatic at different WSHV levels, 700°C, VHSV in ml CH₄/g cat*h
Figure 45: Conversion of methane at different WHSV levels, 700°C, VHSV in ml CH₄/g cat*h
Figure 46: Temperatures of two mass loss processes (Peak 1 and Peak 2) and total mass loss in wt.%

Figure 47: H/C molar ratio of the coke after reactions at different WHSV level.
3.3.6 Temperature influence on catalytic performance

The temperature influence on the catalytic performance was investigated. The reactions were performed in a fixed-bed reactor. As it can be seen in Figure 48, aromatic yield increases by increasing of reaction temperature. Higher yields of aromatic were observed for 725°C and 800°C (maximum yields of 9 mol.% and 15 mol.%, respectively) than previously observed at a reaction temperature of 700°C (maximum yield of 7 mol.%). The maxima of aromatic yields given after approximately 60 to 90 minutes TOS. However, there is very strong drop in product yield after 180 minutes TOS was detected. This fact was not observed in previous results in fixed bed reactor.

The catalyst behavior changes markedly for reaction temperature of 850°C. A maximum yield of 12.8 % was achieved, afterwards the aromatic formation declines significantly. After 160 minutes TOS, no further aromatic were formed. This catalyst was regenerated under normal conditions, and put through a second experimental cycle. No aromatic were formed in this second cycle.

Figure 49 represent the results of TGA analysis of the coked catalyst. The temperature of the maximum mass loss and the amount of the burned coke are shown. The temperature needed to burn out the coke increases with increased reaction temperature. That indicates on the intensification of the formation of high-condensed nearly graphitic-like coke on the catalyst, which can not be burned off. Also almost three times more coke have been formed at 800°C than at 700°C. This may be the reason for rapid deactivation of the catalyst at 800°C (sharp slope for 800°C curve after maximum) that can be seen on Figure 48.
Figure 48: Total aromatic yield for the conversion of methane over Mo/HZSM-5 for reaction temperatures of 700°C, 725°C, 800°C and 850°C.

Figure 49: Coke total mass loss (secondary axe), peaks mass loss temperatures and H/C ratio of the coke (secondary axe) at different reaction temperatures.
3.3.7 Influence of CO₂ presence on catalytic performance

3.3.7.1 Fixed bed results

The total aromatic yield and molar aromatic distribution of benzene for the fixed bed reactions under varying amounts of carbon dioxide added to the methane feed stream is illustrated in Figure 50 and Figure 51. The reactions were performed with high WHSV at 3.7 h⁻¹ due to the very low flow of CO₂ needed and corresponded limitation of Mass Flow Controllers (MFC) for it. Benzene, naphthalene and toluene were the only other aromatic products regularly detected, consistent with previous results. No heavier compounds were detected during the reactions.

Figure 50 shows that with the high flow rate of methane, addition of carbon dioxide is detrimental to aromatic formation over longer periods of time on stream. An addition of 5 mol.% carbon dioxide effects aromatic yield to a greater extent than at lower concentrations. With such an addition of carbon dioxide, maximum aromatic formation is seen to take approximately 30 minutes longer on stream than at lower concentrations, shown above by the rightward shift of the yield. This is in agreement with some works which were not able to detect positive CO₂ influence on the catalytic performance, e.g. [133]. Other researchers reported some decrease of aromatic formation, but improve of long term catalyst stability due to the coke removal by reaction with CO₂ to form CO, e.g. [85, 86]. As stated in [134] and in [135] carbon dioxide can oxidize active MoCₓ species instead of carbon deposits. CO₂ dissociates at carbon vacancies to form a steady-state concentration of chemisorbed oxygen at carbide surfaces. And high thermodynamic activity of the chemisorbed oxygen can lead to Mo₂C oxidation to less reactive MoOₓ species.

It can be seen in Figure 51 that the addition of carbon dioxide does improve selectivity towards benzene. Almost similar behavior of benzene selectivity was observed in the first 60 minutes on stream. After that reaction time benzene selectivity remain at the level of 90-92 mol.% in case of only methane as a feed. The addition of carbon dioxide increases the long-term selectivity from 91% to approximately 96%. The percentage of carbon dioxide within the feed stream appears to be unimportant with regards to this promoted selectivity; the mere presence of carbon dioxide seems to be sufficient to provide such a behavior. Although not shown, toluene and naphthalene selectivity decreased by approximately the same proportion.
Figure 50: Total aromatic yield for the conversion of methane over Mo/HZSM-5 for reaction conditions of 3.7 g CH\textsubscript{4}/g Cat*h with varying amounts of carbon dioxide added to the methane feed. Each reaction has been performed with a fresh catalytic bed.

Figure 51: Molar aromatic distribution of benzene for reaction conditions of 3.7 gCH\textsubscript{4}/g cat*h with varying amounts of carbon dioxide added to the methane feed. Each reaction has been performed with a fresh catalytic bed.
3.3.7.2 Fluidized bed results

Figure 52 represents yields from fluidized bed reactor using 3 mol.% of CO₂ as co-feed to methane. Other fluidized bed experiments without CO₂ are given for comparison reasons. The reaction conditions are 700°C, 3% of CO₂ in the feed, WHSV=1 h⁻¹. As it can be seen, similar to the results described in Chapter 3.3.3.1 highest yield was achieved due to the increased naphthalene production, as shown in the Figure 53.

Similar to the fixed bed the presence of the carbon dioxide hinders the MDA. This concerns both the maximum of achieved yields and the yields over longer TOS.
3.3.8 Physical mixtures of Mo₂C and Mo/HZSM-5

Catalysts with the following Mo load were investigated:

- 2.5 wt.% Mo₂C and HZSM-5 physical mixture,
- 4.0 wt.% Mo₂C and HZSM-5 physical mixture,
- 5.5 wt.% Mo₂C and HZSM-5 physical mixture,

The physical mixture of HZSM-5 with Mo₂C load of 2.5 wt.% was tested at 700°C and 800°C. No catalytic activity was observed. However, a lot of coke formation was detected, around 4.0 mass.% of the spent catalyst. The coke was burned out at wide temperature range 380-550°C.

The catalyst with 4 wt.% and 5.5 wt.% of Mo₂C showed relative high activity level. The Figure 54 represents the yields of reactions with different concentrations of Mo₂C. The reaction conditions are 700°C, WHSV=4.3 h⁻¹, VHSV=6000 mlCH₄/g Cat*h. It can be seen that increased load of Mo₂C (from 4 to 5.5 mass.%) leads to increase of methane conversion (i.e. aromatic yield, because selectivity is approx. 100 %) from 1.5 to 3 mol.%. But the results are
still below the activity of impregnated 4% Mo/HZSM-5 catalyst which converts around 4 mol.% methane after 30 min reaction time. The reason for moderate activity of Mo\textsubscript{2}C and HZSM-5 physical mixtures probably is a limited contact of these substances by building of active species (low specific surface of Mo\textsubscript{2}C particles). In case of impregnated catalyst this problem is not present.

![Graph](image)

**Figure 54**: Physical mixtures of Mo\textsubscript{2}C and HZSM-5, Mo/HZSM-5 results are given for comparison. Yields of aromatic in mol.% Conditions: methane WHSV=4.3 h\textsuperscript{-1}, 700°C, aromatic selectivity=100%.

### 3.3.9 Conclusions and Outlook

Mo-HZSM-5 with is very selective catalyst for producing of aromatic. The liquid reaction products contain up to 95% of benzene and toluene as well as naphthalene. Selectivity to benzene increases at longer TOS to 90-95 mol.%. In case of fluidized bed reactions increased up to 20% formation of the naphthalene was observed.

Higher yields of aromatic can be achieved in fluidized bed reactor (6.3 mol.% vs. 5.5 mol.% compared with fixed bed reactor or increase of 15 %). Better mix behavior of fluidized bed reactor favors the better gas-solid contact and facilitates the reaction. Furthermore better heat
transfer in fluidized bed prevents the formation of “hotspots” – local overheated areas. It is more important during oxidative regeneration of the catalyst. However, a strong particles size reduction due to the attrition was observed and a long-term deactivation of the catalyst occurs faster than in fixed bed. Significant changes in the catalyst properties and structure were detected after use in the fluidized bed.

In case of improved mechanical stability of catalyst particles fluidized bed reactor can be successful applied for performing of MDA reaction. It cannot be ruled out that moderate increase of the reaction temperature will be possible also (up to around 750°C).

The optimum of methane WHSV is around 1.4 – 2.0 h\(^{-1}\) (approx. 2000 – 2800 ml CH\(_4\)/g cat* h). Higher WHSV lead to the fast deactivation of the catalyst due to the strong coke formation. If continuous regeneration of the catalyst will be applied in fluidized bed reactor, further increase of WHSV up to 4 h\(^{-1}\) (6000 ml CH\(_4\)/g cat*h) and more will be possible.

The temperature has very strong influence on the reaction procedure. The catalyst becomes active from approx. 973 K and continuously increases the aromatic production till approx. 1073 K. Indeed the strong coke formation was detected also, which results in faster catalyst deactivation. At 850°C no further raise of aromatic yield can be observed and complete deactivation of catalyst occurs. No regeneration is possible.

Carbon dioxide has a detrimental influence on the catalytic properties of Mo/HZSM-5. The physical mixture of molybdenum carbide and HZSM-5 can be used for MDA but have lower activity and long-term stability properties.

A positive effect of the catalyst hydrogen pretreatment could not be detected.

Further optimization of the reaction parameter as well of the catalyst properties is necessary to perform MDA reaction economically in the large industrial scale.
3.3 Dimethyl Carbonate Production

3.3.1 Overview and Definitions

The reactions were performed in the liquid and in the gas phase. A stirred reactor was used for the liquid phase reactions and the gas phase reactions were performed in the fixed bed reactor. The Figure 55 and Figure 56 represent flow sheet diagram for fixed bed reactor and the picture of the reactor set up. Please refer for the detailed information to the Chapter 5.1.3 - Fixed bed reactor for DMC production.

Figure 55: Flow sheet diagram of fixed bed reactor for propylene carbonate/methanol transesterification

Figure 56: Fixed-bed reactor set up
Definitions for Propylene Carbonate (PC) conversion, Dimethyl Carbonate (DMC) and Propylene Glycol (PG) yield and selectivity are presented in Equations 29-31. All calculations have PC as a referent substance due to the excess of methanol used.

\[
\text{PC conversion (mol\%)} = \frac{\text{mol PC out}}{\text{mol PC in}} \times 100\% \tag{29}
\]

\[
\text{DMC (PG) yield (mol\%)} = \frac{\text{mol DMC (PG) out}}{\text{mol PC in}} \times 100\% \tag{30}
\]

\[
\text{DMC (PG) selectivity (mol\%)} = \frac{\text{mol DMC (PG) out}}{\text{mol PC in} - \text{mol PC out}} \times 100\% \tag{31}
\]

Chemical reaction of PC and MeOH transesterification is shown on Eq. 32. As it can be seen same quantity of PG moles are formed during DMC production. So it is important to achieve high PG selectivity during the reaction and not only high selectivity to DMC.

\[
\text{PC} + 2\text{CH}_3\text{OH} \rightarrow \text{MeO} - \text{C} - \text{OMe} + \text{Me} \begin{array}{c} \text{OH} \\ \text{OH} \end{array} \tag{32}
\]

Data concerning the boiling point of the reaction participants and its danger classes are given in Annex 1. Methanol has the lowest boiling point of 65°C, this is the reason (as well as boiling point of DMC/MeOH azeotrope) which restricts higher temperature level during performing this reaction in liquid phase. The PC has the highest boiling point of 242°C, what make it difficult to perform this reaction in vapor phase at normal pressure due to the high reactivity/cracking reactions of the reaction mixture in the presence of catalyst.
3.3.2 Liquid phase reactions

3.3.2.1 Propylene Carbonate and Methanol Transesterification

Reactions in liquid phase were performed in order to test different catalysts like zeolites and metal oxides on its suitability for transesterification of methanol and propylene carbonate. An overview on the reaction conditions is given in Table 14. Methanol excess was used to shift the reaction equilibrium in the side of reaction products. Temperature of 60°C is the highest temperature at which reaction components still remain in liquid phase.

<table>
<thead>
<tr>
<th>Table 14: General overview on reaction conditions in liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol / Propylene Carbonate molar ratio</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Catalysts amount</td>
</tr>
<tr>
<td>PC amount</td>
</tr>
<tr>
<td>Reactor type</td>
</tr>
</tbody>
</table>

The next Table 15 represents the screening of different catalysts. As it can be seen zeolites are not active in liquid phase for this reaction. However, some metal oxides as well as hydrotalcites showed high activity.

Interesting is the activity of metal oxides in the group IIA of periodic table: MgO-CaO-SrO-BaO. Figure 57 represents activity comparison of these oxides. The values after around 20 min reaction time are shown. It can be seen that all of oxides are very selective to desired DMC and PG. MgO has a moderate activity and gives around 17 mol.% PC conversion with 86 mol.% selectivity to DMC. CaO was able to convert ca. 70 mol.% of PC with 98.5 % selectivity to DMC. However, the catalytic activity of SrO and BaO showed decreased tendency and the conversions were 60 and 48 mol.%, respectively. The reason for this behavior is possibly molecular radius and the correspond differences in the ability to activate the MeOH molecule.

The catalysts basicity can be determined by CO$_2$-TPD analysis. Figure 58, Figure 59, Figure 60 and Figure 61 show CO$_2$-TPD of these oxides. It can be seen, that CaO in contrast to other oxides has strong basic sites and their very narrow distribution. This seems to be a reason for its high activity for this reaction and the highest selectivity to DMC and PG.
Table 15: Catalysts screening in liquid phase

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PC conversion, %</th>
<th>DMC selectivity, %</th>
<th>DMC yield, %</th>
<th>PG selectivity, %</th>
<th>PG yield, %</th>
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</thead>
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<tr>
<td>BLANK</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZrPO₄</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>H-Beta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B-MFI</td>
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<tr>
<td>MoO₃</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>3</td>
<td>16</td>
<td>0.5</td>
<td>90</td>
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</tr>
<tr>
<td>PrO</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H-Talcite</td>
<td>28</td>
<td>93</td>
<td>26</td>
<td>96</td>
<td>27</td>
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<tr>
<td>Amberlyst A26 OH</td>
<td>2.8</td>
<td>36</td>
<td>1.0</td>
<td>89</td>
<td>2.5</td>
</tr>
<tr>
<td>MgO</td>
<td>17</td>
<td>86</td>
<td>14.7</td>
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<td>16</td>
</tr>
<tr>
<td>CaO</td>
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</tr>
<tr>
<td>BaO</td>
<td>48</td>
<td>98</td>
<td>47</td>
<td>92</td>
<td>44</td>
</tr>
</tbody>
</table>

MgO presented big amount of relative weak basic sites at 400°C and fewer amounts of stronger sites, which were desorpted at 500°C and 800°C. This corresponds to the limited PC conversion and DMC selectivity of MgO-catalyst during reaction performing.

SrO has very strong acid sites with desorption temperature over 800°C - Figure 59. However, the catalytic results of SrO were second best after CaO, around 60 mol.% of PC conversion at 98 mol.% DMC selectivity. PG selectivity of SrO was the second lowest from considered oxides at the level of 87 mol.%.

BaO has few CO₂-desorption peaks at 400°C, 680°C and 740°C - Figure 60. BaO presented one of the lowest PC conversion rates of 48 mol.% and high DMC selectivity. PG selectivity was moderate at the level of 92 mol.%.

So, CO₂-TPD can be used for the estimation of catalytic properties, but some aspect of catalysis can not be explained by this analysis.
Figure 57: Overview on MgO-CaO-SrO-BaO activity. PC conversion, selectivity to DMC, DMC yield, PG selectivity and PG yield are shown.

Figure 58: CO$_2$-TPD analysis of MgO
Figure 59: CO$_2$-TPD analysis of SrO

Figure 60: CO$_2$-TPD analysis of BaO
3.3.2.2 Use of superbases Na/NaOH/MgO

The superbases Na/NaOH/MgO were tested as catalysts for the PC/methanol transesterification. Very high catalytic activity was detected. No other products apart desired DMC and PG were detected in the reaction mixture (and unconverted PC and MeOH). So selectivity to DMC and PG was close to 100%.

Different content of Na and NaOH was used to find optimal concentrations of these ingredients in the superbase. “Design Expert 5” program was used to optimize these parameters and make visualization of used concentrations and its effect. The response surface with 3 level factorial design was built finally. Both cubic and quadratic models were used.

First, an experiment table was made to determine experiments to be performed. Also some additional experiments were performed from redundant reasons. These additional experiments can be integrated in the final response surface and make the entire results more precise. All experiments as well as “response” – yield of DMC are shown in Table 16: Experiments list.
for building of response surface. Na and NaOH concentrations are given in mmol substance per g support (MgO).

Table 16: Experiments list for building of response surface, DMC selectivity around 100 mol.% for all experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>NaOH (mmol/g)</th>
<th>Na (mmol/g)</th>
<th>PC conversion / DMC yield (mol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>31.5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>4</td>
<td>48.8</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>4</td>
<td>71.1</td>
</tr>
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<td>6</td>
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<td>2</td>
<td>50</td>
</tr>
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<td>4</td>
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<td>10</td>
<td>2.5</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>14</td>
<td>2.5</td>
<td>2.2</td>
<td>55</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>4.3</td>
<td>52</td>
</tr>
<tr>
<td>16</td>
<td>1.3</td>
<td>3.5</td>
<td>49</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>3.5</td>
<td>69</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>1</td>
<td>20</td>
</tr>
</tbody>
</table>

After that, response surfaces can be formed by using “Design Expert 5” software. Figure 62 represents response surfaces using quadratic model. Axis X is the NaOH concentration in superbase and axis Y – these of Na. Responses are shown in form of contours. These contours represent combination of both factors – Na and NaOH concentrations – that result in the same level of DMC yield.

As it can be seen DMC yield grows continuously by increasing of Na and/or NaOH concentrations in the superbase. Also it can be realized that at higher NaOH and Na concentrations (2-4 mmol/g) stronger influence of Na concentration can be seen. This means effect of small increase of Na is higher then effect of same increase of NaOH content. Graphically this is shown by curves tendency to be more horizontally at higher concentrations.

Next Figure 63 represents the response surface in a cubic model. The general tendency of factor influence is the same as in quadratic model, but cubic model is more precise. As it can be seen, at higher concentrations further increase of NaOH doesn’t improve DMC yield. E.g. DMC yields at the point 2:4 (NaOH:Na concentration) and 4:4 are equal. Contour 72 % represents maximum of the real
yields, which can be achieved in liquid phase with 8:1 methanol excess. Further increase of Na and NaOH don’t lead to an yield (i.e. PC conversion, selectivity remain around 100 mol.%) improvement.

Attempts to reuse the catalyst after reaction resulted in very low yields at the level of 3-5 mol.%. This is an indication that Na-species in the catalyst are labile and are been leached during reaction. And Mg-framework without Na-species leads only to a limited PC conversions at high selectivities around 86 mol.% - Table 15: Catalysts screening in liquid phaseTable 15. So it can be assumed that catalysis had a homogeneous character because of the leaching of Na-species from the MgO support.

3.3.2.3 Propylene Carbonate and Phenol Transesterification

Study about possibility of transesterification of PC and PhOH, as shown in Equation 33, was carried out. In this reaction propylene carbonate reacts with phenol to diphenyl carbonate (DPC) and propylene glycol.

\[
\text{MeOC}=O + 2 \text{PhOH} \rightleftharpoons \text{PhO} \text{C} \text{OPh} + \text{HO} \text{CMe} \text{OH}
\]  

(33)
Table 17 represents the reaction conditions.

<table>
<thead>
<tr>
<th>Phenol / Propylene carbonate ratio</th>
<th>8:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>60°C</td>
</tr>
<tr>
<td>Catalysts amount</td>
<td>0.15 g</td>
</tr>
<tr>
<td>PC amount</td>
<td>35 mmol (3.5 g)</td>
</tr>
<tr>
<td>Reactor type</td>
<td>liquid phase, stirring reactor, 900 rpm</td>
</tr>
</tbody>
</table>

Different catalysts which performed good activity in PC / MeOH transesterification were tested. No PC conversion and/or DPC and PG in the reaction products were detected. Table 18 gives overview on used catalysts and results. The possible reason for such behavior of catalyst can be both a steric hindrance of big PhOH molecule and its unfavorable chemical activity in the first reaction step during PhOH activation by the catalyst (as in Chapter 2.5.4 described). Also other researchers, e.g. [130] pointed out that direct synthesis of DPC from EC and PhOH is not thermodynamically favorable (and reactions with EC are easier to perform, than with PC – Chapter 2.4.2).

Table 18: Catalyst used for PC/PhOH transesterification and results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PC conversion, %</th>
<th>DMC yield, %</th>
<th>PG yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CaO 60°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BaO 120°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HT 120°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BMFI 300°C, 30 min</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 3.3.3 Gas phase reactions

#### 3.3.3.1 Definitions and reaction conditions

Most of the data about reaction conditions are shown in Table 19. The molar excess of methanol was 6 (molar ratio MeOH/PC = 6:1), a temperature range from 250°C to 350°C was used because of very high boiling point of PC - 242°C as in Annex 1 presented. Thus, the reactions had have to be performed over this temperature to be sure, that there are complete vapor phase conditions present. At the temperatures over 350°C strong side products formation was detected, vide infra.
### Table 19: Gas phase reaction conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol / Propylene Carbonate molar ratio</td>
<td>6:1</td>
</tr>
<tr>
<td>Temperature range</td>
<td>250-350°C</td>
</tr>
<tr>
<td>Catalysts amount</td>
<td>around 2 g</td>
</tr>
<tr>
<td>Residence time</td>
<td>0.1-2 s</td>
</tr>
<tr>
<td>Reactor type</td>
<td>fixed-bed, metal coil tube reactor</td>
</tr>
</tbody>
</table>

Contact time was defined as in **Equation 34** shown. Total gas flow consisted from MeOH, PC and nitrogen as a carrier gas.

\[
\text{Contact time (s)} = \frac{\text{catalyst bed volume (m}^3\text{)}}{\text{total gas flow at reaction temperature (m}^3\text{/s)}} \tag{34}
\]

PC conversion, DMC and PG yield and selectivity are defined as already in **Chapter 3.3.1** represented.

### 3.3.3.2 Catalysts screening in fixed bed reactor

One of the best catalyst – ZrPO₄ – for cyclic carbonates cleavage as in [136] reported was tested in gas phase in a fixed bed reactor at ambient pressure. Also the catalyst having highest activity in the liquid phase reactions were tested as well. Reaction conditions are: 300°C, 0.5 and 1.5 s reaction time, VHSV ca. 15000 ml/g*h.

Table 20 represents the results. The blank experiment (glass balls were used) didn’t lead to any formation of desired products, see Figure 64. As it can be seen, almost all catalysts presented high conversion rates at both 0.5 s and 1.5 s contact times. However, the selectivity to desired products remains very low. A lot of different side products were detected in the reaction mixture. It was not possible to found more details about nature of side products because of the many peaks and its narrow distribution. It can be assumed, that strong acid sites of used zeolites lead to the destruction of the PC molecule and to the numerous side reactions. Also CaO showed surprisingly high PC conversion rate. This show that also basic sites can effective cleave PC molecule at 300°C what is in agreement with [136].
Table 20: Gas phase reaction conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PC conversion, % at 0.5s/1.5s</th>
<th>DMC yield, % at 0.5s/1.5s</th>
<th>DMC selectivity, % at 0.5s/1.5s</th>
<th>PG yield, % at 0.5s/1.5s</th>
<th>PG selectivity, % at 0.5s/1.5s</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>1/1.5</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
</tr>
<tr>
<td>H-Beta</td>
<td>60/95</td>
<td>16/5.3</td>
<td>27/5.6</td>
<td>0/0.2</td>
<td>0/0.2</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>100/99</td>
<td>0/12.2</td>
<td>0/12.4</td>
<td>0/16.7</td>
<td>0/16.9</td>
</tr>
<tr>
<td>ZrPO4</td>
<td>100/100</td>
<td>0.75/0</td>
<td>0.75/0</td>
<td>0.74/0</td>
<td>0.74/0</td>
</tr>
<tr>
<td>B-MFI</td>
<td>20/97</td>
<td>1.6/1.6</td>
<td>8.1/1.7</td>
<td>2.1/0</td>
<td>10.6/0</td>
</tr>
<tr>
<td>CaO</td>
<td>36/95</td>
<td>1.8/7.8</td>
<td>6/8.2</td>
<td>4/0.35</td>
<td>12/0.36</td>
</tr>
</tbody>
</table>

Figure 64: GC of the reaction mixture after blank experiment (300°C, 1s reaction time).

The catalyst HZSM-5 showed high selectivity to several compounds. Reaction mixture had an intensive smell of diesel fuel. GC-MS analysis of reaction mixture showed presence of large amount of different aromatic compounds, some of them are presented in Figure 65. Obviously HZSM-5 catalyst led to the conversion of methanol to the components of gasoline fuel, which is relative well known so called “Mobil process” [137].
3.3.3.3 Use of Y-zeolites

Cu loaded Y-zeolites are reported as an effective catalyst for “one pot” synthesis of dimethyl carbonate from propylene oxide and carbon dioxide, e.g. [138, 139]. This reaction goes in two steps as in Chapter 2.5.2 described. Copper is responsible for the activation of the CO$_2$ molecule and zeolite supports both reactions. The idea of the follow work was to use Y-zeolites for PC and MeOH gas phase transesterification to DMC and PG at ambient pressure in fixed bed reactor. Y-zeolites (FAU structure) with different Si/Al ratio and ionic form were chosen as starting material for catalyst preparation. The full list of the used supports and prepared catalysts can be found in Experimental Part, Chapter 5.3 Catalysts. Calcination atmosphere and time, press time and pressure as well as different reaction parameters were varied to optimize reaction conditions.

3.3.3.3.1 Estimation of the reaction parameters

Before starting the tests of the different Y-catalysts, estimation of reaction parameters was carried out. This means reaction temperature and contact time. One support – CBV 400 – was chosen to find roughly the optimum of the reaction conditions. The main idea at the start of experiments was that shorter contact times of the reaction educts and catalyst bed will favor higher selectivity to the desired DMC and PG. As it is shown above in Chapter 3.3.3.2 strong destruction of the PC was observed during use of zeolites at 300°C and contact times 0.5/1.5s.

Figure 66, Figure 67 and Figure 68 show PC conversion, DMC selectivity and yield at different contact times at 300°C. An important observation was the absence of the PG peak in the reaction mixture. This problem will be discussed in the next Chapter 3.3.3.2. In terms of PC conversion applied contact times showed almost same activity in the range of 30-45 mol.%. Longer contact time of 0.15s lead to better yields and especially better selectivity.
Around 16 mol.% DMC selectivity was observed at 0.15 s contact time against only 8 mol.% if 0.025 s contact time was used, see Figure 67.

So some longer residence time was used for the next experiments at 330°C. Figure 69, Figure 70 and Figure 71 represent the results. Again the longest contact time of 0.35 s resulted in the best DMC yield. The selectivity to DMC was also higher at longer contact time, except the shortest 0.03s. In this case some increase of DMC selectivity was observed, Figure 69. However, the lowest PC conversion at this contact time was detected (less than 10 mol.% after 80 min TOS). For other contact times continuously reducing of PC conversion was detected. After 80 min TOS around 50 mol.% of PC conversion was observed. However, at the reaction start up to 90 mol.% PC conversion was found for reaction with 0.35 s contact time and around 65 mol.% for the 0.08 s. So deactivation of the catalyst equalizes the differences in the PC conversion after around 80 min TOS.

Figure 66: PC conversion at different contact times, 300°C
Results and Discussion – Dimethyl Carbonate Production

Figure 67: DMC selectivity at different contact times, 300°C

Figure 68: DMC yield at different contact times, 300°C
Figure 69: PC conversion at different contact times, 330°C

Figure 70: DMC selectivity at different contact times, 330°C
The next step was the estimation of the reaction temperature. The used contact time was 0.15s and three temperatures were tested: 300°C, 330°C and 370°C.

The following Figure 72, Figure 73 and Figure 74 represent PC conversion, DMC yield and selectivity, respectively. It can be seen, that PC conversion is relative stable at 300°C, but at 330°C it decreases more sharply and at 370°C this process becomes dramatic character. The selectivity to DMC drops continuously at 300°C. At 330°C it has an maximum at 15 mol.%. However, surprisingly high selectivities were observed at higher temperatures. The temperature and reaction time have positive effect on DMC selectivity, at 370°C around 22 mol.% of DMC was detected in the reaction mixture. In contrast to the selectivity at lower temperatures, it seems that catalyst at 370°C is too active at starting the reaction. It converts almost all of PC to the side products at the beginning. And after that some deactivation occurs which leads to the increase of the DMC formation. However, in terms of yield DMC formation increases continuously at 370°C, see Figure 74.

So optimal reaction temperature seems to lie in the range 330-350°C and contact time 0.2-0.5 seconds. These parameters will be used for the comparison of different catalysts and for fine-tuning of the reaction conditions.
Figure 72: PC conversion at different temperatures, 0.15 s contact time

Figure 73: DMC selectivity at different temperatures, 0.15 s contact time
No PG could be detected in the reaction mixture. In order to detect stability of PG at higher temperatures the following experiments were performed: PG and DMC (molar ratio 1:1) as starting reaction material, temperatures 200, 250 and 300°C, catalysts: H-Beta-, BMFI- and Y-zeolite. Reaction conditions: contact time 0.1s, VHSV=18000 ml/g*h. Table 21 represents the results. As it can be seen, already reaction temperatures of 200°C lead to the complete PG destruction if H-Beta is used as catalyst. Moreover, further temperature increase to 250°C and 300°C has a complete PG destruction as well partial or complete DMC molecule splitting as a result. BMFI and Y-zeolite don’t destroy PG molecule at 200°C; at 250°C around 50% of PG was cleaved and at 300°C all of PG was disappeared from the reaction mixture. So it can be concluded, that the reaction performing in the gas phase at the present conditions can not lead to the PG formation. Possibly performing of this reaction at lower pressures and temperatures will solve this problem. Also use of the shorter contact times was considered as a possible solution, but this doesn’t lead to the formation of the desired products, vide supra.

Figure 74: DMC yield at different temperatures, 0.15 s contact time

3.3.3.3.2  PG absence in the reaction mixture
Table 21: Remained amount in mol.% of DMC and PG after reactions at different temperatures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>200°C DMC</th>
<th>200°C PG</th>
<th>250°C DMC</th>
<th>250°C PG</th>
<th>300°C DMC</th>
<th>300°C PG</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Beta</td>
<td>100</td>
<td>0</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BMFI</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>K-6 (Y-zeolite)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>65</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3.3.3.3 Catalyst screening

Different catalysts were tested for its suitability in the PC/MeOH transesterification. All catalysts were calcined in air atmosphere at 500°C for 4 h and then pressed at 10 tons and 30 min. Used particles size was 0.5-1.6 mm. Reaction conditions: 330°C, 0.3 s contact time, VHSV=1800 ml/g*h. The full list of used catalysts and its preparation procedure can be found in Chapter 5.3.

Figure 75 and Figure 76 represent the results and Figure 77 gives an visual overview on achieved PC conversions and DMC selectivities as a function of Si/Al ratio of the used catalysts (average values after 120 min reaction time are given). Most of the catalysts were able to convert 50-70 % of PC during at least 120 min reaction time. Interesting is the difference between activity of K-6 and K-15 catalysts. Both have Si/Al ratio of 5.2, but K-6 is an H-form and K-15 is a NH$_4$-form of the zeolite. It can be seen that NH$_4$ form of zeolite achieves better PC conversion during longer time period (around 10 mol.% more PC conversion – see Figure 75). Some better DMC selectivity can be achieved using the zeolite in the H-form, but already after 120 min TOS both catalyst show same selectivity level at around 20 mol.%.

The best results were achieved by catalyst K-8 and K-9, which have Si/Al ratio of 11.5 and 30, respectively. The three lowest conversions are produced by catalysts with lowest Si/Al ratio (K6-5.2; K15-5.2; K14-6.0). Low Si/Al ratio results in the relative small amount of very strong Lewis acid sites and lead to the strong activity of the catalyst at the reaction start. However, rapid deactivation of catalyst occurs. Thereagainst, catalysts with high Si/Al ratio have relative much weak acid sites. This results in the more stable PC conversion at longer
TOS. Already after short reaction time of 30 min catalysts with high Si/Al ratio achieve more PC conversion – see Figure 75. Further increase of the Si/Al ratio of the zeolite leads to the PC conversion drop. So an optimum of Si/Al ratio was found which can be seen at Figure 77. Two catalysts with moderate Si/Al ratio of 11.5 and 30 achieved best PC conversion over the used reaction time. Too strong acid sites show high activity at the reaction start but then it continuously drops from initial value of 95 mol.% to around 70 mol.% (after 40 min TOS) due to the strong catalyst deactivation. Too weak acid sites are not able effectively convert PC and show moderate activity even at the reaction start, see Figure 75.

A similar tendency was observed in terms of DMC selectivity: too strong or too weak acid sites lead to lower selectivity. However, catalyst with Si/Al ratio of 5.2 showed relative high DMC selectivity at the reaction beginning, which sank after some reaction time. So same Si/Al ratio optimum (i.e. Si/Al range = 10-30) exists, if selectivity to DMC is considered over longer time period – see Figure 76 and Figure 77. Up to 25 mol.% DMC selectivity was observed if catalyst with Si/Al ratio of 30 was used.

The catalytic results of two catalysts in the Na and Ca ionic form (K-11 and K-13) will be presented in Chapter 3.3.3.3.11. Completely other reaction products were detected in case of these two catalysts.
Figure 75: PC conversion, 0.3 s contact time, 330°C
Figure 76: DMC selectivity, 0.3 s contact time, 330°C
3.3.3.4 Particle size effect

Effect of particle size was investigated. Catalyst was calcined in air atmosphere at 500°C for 4 h, then pressed at 10 tons during 30 min. Reaction conditions: 330°C, 0.3 s contact time, VHSV=1800 ml/g*h. Catalyst K-9 was used. Particles with mesh size of 0.5-1.6 mm were sieved to three fractions: 0.4-0.7 mm, 0.7-1.0 mm, 1.0-1.6 mm.

Figure 78 and Figure 79 represent the achieved results. The broadest fraction 0.5-1.6 showed the best results in terms of both conversion and selectivity. No positive effect of the narrowing of particles size distribution to the 0.4-0.7 mm range could be detected. Except the biggest particles all particles ranges presented nearly same activity level in terms of PC conversion and DMC selectivity. It can be concluded that below 1 mm particle size the reaction rate is not limited by the transportation of the PC and methanol to the pores as well as by desorption and transportation of the reaction products from the catalysts pores. Only if the biggest particles of 1.0 – 1.6 mm were used the DMC selectivity drops to the values of 15 mol.%. The reason for the high activity of broad fraction was possibly that the big particles
optimized the gas flow within the catalyst bed and hence led to the better total catalyst activity.

Figure 78: PC conversion, 0.3 s contact time, 330°C

Figure 79: DMC selectivity, 0.3 s contact time, 330°C
3.3.3.3.5 Temperature effect

As shown above (Figure 72, Figure 73, Figure 74), temperature has a strong influence on the reaction. Fine temperature tuning was done to investigate this effect more precisely. The catalyst was calcined in the air atmosphere at 500°C for 4 h, then pressed at 10 tons during 30 min. Reaction conditions: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, VHSV=1800 ml/g*h. Catalyst K-8 was used.

If the temperature increases from 320°C to 330°C some better PC conversions can be achieved (see Figure 80), whereas the DMC selectivity remains at the level of around 20 mol.% (see Figure 81). Also the DMC yield grows by around 4 mol.% (Figure 82). Further temperature increase doesn’t lead to a significant improvement of the reaction parameter. The conversion remains at the level of about 75 mol.% after 2.5 h reaction time and small selectivity decrease of about 3 mol.% can be observed.

Too low temperatures are not enough to perform desired reaction (i.e. to convert PC) and too high temperatures lead to the formation of side products/cracking reactions. So the optimum of the reaction temperature is around 330°C.

![Figure 80: PC conversion, 0.3 s contact time.](image-url)
Figure 81: DMC selectivity, 0.3 s contact time.

Figure 82: DMC yield, 0.3 s contact time.
3.3.3.3.6 Pressing time effect

The catalyst powder forms hard tablets during pressing, which have been crushed afterwards to the necessary particle size. Pressing has an effect in reducing of catalyst pores and as a consequence of BET and micropore area and volume. This can be seen in Table 22. As a result of these catalyst structure modifications its activity was changed significantly, too. Figure 83 and Figure 84 illustrate that after 10 and 30 min pressing time the catalyst achieved similarly high activity of around 30-35 mol.% DMC selectivity (with a maximum of 46 mol.% in case of 30 min pressing) and continuously reduced conversions from 80 mol.% to 30 mol.% after 5 hours reaction time. Thereagainst, long pressing time led to a strong activity drop of the catalyst in respect to DMC selectivity. PC conversion was slightly higher than after 10 and 30 min pressing. This is an indication that catalyst micropores are of primary importance for the performing of reaction and DMC formation. Reaction conditions: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, VHSV=1800 ml/g*h.

So it can be seen that pore size plays an important role in this reaction. Increased pressing time from 10 min to 30 min leads to the small changes in the catalyst structure (decrease of BET and micropore area) and to the some increase of DMC selectivity. Further micropores destruction by catalyst pressing during 2h causes stronger PC conversion on unchanged macropores of the catalyst with low DMC selectivity.

Table 22: BET and micropore area and volume reducing during catalyst pressing at 10 tons during different times, calcination temperature is 500°C.

<table>
<thead>
<tr>
<th>Pressing time in min</th>
<th>BET in m²/g</th>
<th>Micropore area in m²/g</th>
<th>Micropore volume in cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>644</td>
<td>472</td>
<td>0.2321</td>
</tr>
<tr>
<td>30</td>
<td>637</td>
<td>467</td>
<td>0.2264</td>
</tr>
<tr>
<td>120</td>
<td>609</td>
<td>437</td>
<td>0.2117</td>
</tr>
</tbody>
</table>
Figure 83: PC conversion, 0.3 s contact time, 330°C

Figure 84: DMC selectivity, 0.3 s contact time, 330°C
3.3.3.7 Pressing pressure effect

Influence of applied pressure for catalyst press was studied. Three different pressures of eight, nine and ten tons were applied. Pressing time was constant during all experiments at the level of 10 min. Changes in the catalyst structure after pressing in terms of BET, micropore area and volume were measured and are given in Table 23. As it can be seen, no significant changes were detected. Some loss of BET area from initial value of 698 m$^2$/g to 667 m$^2$/g after pressing at 8 tons and to 644 m$^2$/g after pressing at 10 tons was observed. Micropore area and volume decreased insignificantly by pressing at 10 tons compare to pressing at 9 tons. However, strong changes in the catalyst activity catalyst were detected in case of “10 tons” catalyst. Its ability to convert PC was significantly lower than that of the two other catalysts – see Figure 85. However, the activity of the “10 tons” catalyst was markedly higher than activity of two other in terms of DMC selectivity – see Figure 86. DMC selectivity of around 33 mol.% was achieved after 150 min TOS during next 150 min. The chosen reaction conditions are: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, VHSV=1800 ml/g*h. The described behavior is untypical and can not be explained by reducing of micropore area and increase of macropores proportion.

Table 23: BET, micropore area and volume after catalyst press during 10 min at different pressures, calcination temperature is 500°C.

<table>
<thead>
<tr>
<th>Pressure in tons</th>
<th>BET in m$^2$/g</th>
<th>Micropore area in m$^2$/g</th>
<th>Micropore volume in cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>After calcination</td>
<td>698</td>
<td>518</td>
<td>0,252</td>
</tr>
<tr>
<td>8</td>
<td>667</td>
<td>496</td>
<td>0,242</td>
</tr>
<tr>
<td>9</td>
<td>646</td>
<td>475</td>
<td>0,232</td>
</tr>
<tr>
<td>10</td>
<td>644</td>
<td>472</td>
<td>0,232</td>
</tr>
</tbody>
</table>
Figure 85: PC conversion, 0.3 s contact time, 330°C

Figure 86: DMC selectivity, 0.3 s contact time, 330°C
### 3.3.3.3.8 Calcination time effect

Increased calcination time reduces normally the amount and size of micropores. This results in the stronger acid sites of catalyst and simultaneously its fewer amounts. Table 24 shows that BET is reduced continuously by increasing the calcination time. Micropore area and micropore volumes are reduced after 240 min calcination time and afterwards grow insignificantly, what can be explained by mistake involved in the applied measurements. The BET surface decreases continuously by increasing of calcination duration. However, there was a clear PC conversion drop in case of 240 min calcined catalyst – see Figure 87. Same catalyst achieved best DMC selectivity of 35 mol.% in contrast to 12-14 mol.% in case of the 1h and 4h calcined catalysts – see Figure 88. Reaction conditions: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, VHSV=1800 ml/g*h. Apparently the small micropores lead to the better DMC selectivity but not to the high PC conversion.

Table 24: BET, micropore area and volume after catalyst calcination at 500°C at three different calcination times, 10 tons pressing pressure during 10 min.

<table>
<thead>
<tr>
<th>Calcination time in min</th>
<th>BET in m²/g</th>
<th>Micropore area in m²/g</th>
<th>Micropore volume in cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>661</td>
<td>492</td>
<td>0,2400</td>
</tr>
<tr>
<td>240</td>
<td>644</td>
<td>475</td>
<td>0,2323</td>
</tr>
<tr>
<td>360</td>
<td>639</td>
<td>477</td>
<td>0,2331</td>
</tr>
</tbody>
</table>
Figure 87: PC conversion, 0.3 s contact time, 330°C

Figure 88: DMC selectivity, 0.3 s contact time, 330°C
3.3.3.3.9 *Calcination temperature effect*

The increase of calcination temperature has normally a similar effect as a calcination time increasing effect. Table 25 demonstrates that a significant loss of the micropore area and micropore volume of the catalyst occurs by increasing of calcination temperature from 450°C to 550°C. BET loss was not as markedly as reducing of micropore area and micropore volume which were found to be a key factors to reach high DMC selectivities. Thereby catalyst activity was affected markedly and the continuous PC conversion drop as in Figure 89 shown was observed. Continuous reducing of BET and micropore area leaded to the decrease of PC conversion. No strong direct dependency between BET surface and catalysts micropores on the one hand and DMC selectivity of the catalyst on the other hand was detected. DMC selectivity remained relative stable at the level of 18 mol.% in case of 450°C and 550°C, and surprisingly strong drop to the value of 12 mol.% was observed if 500°C calcination temperature was applied (Figure 90). So the calcination temperature optimum is over and under the value of 500°C.

As it can be seen significant changes in the catalyst structure by increasing of calcination temperature were able to reduce PC conversion and have only uncertain influence on DMC selectivity.

The reaction conditions are: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, WHSV=1800 ml/g*h.

<table>
<thead>
<tr>
<th>Calcination temperature in °C</th>
<th>BET in m²/g</th>
<th>Micropore area in m²/g</th>
<th>Micropore volume in cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>675</td>
<td>512</td>
<td>0.246</td>
</tr>
<tr>
<td>500</td>
<td>667</td>
<td>496</td>
<td>0.242</td>
</tr>
<tr>
<td>550</td>
<td>667</td>
<td>488</td>
<td>0.238</td>
</tr>
</tbody>
</table>
Results and Discussion – Dimethyl Carbonate Production

Figure 89: DMC selectivity, 0.3 s contact time, 330°C

Figure 90: DMC selectivity, 0.3 s contact time, 330°C
3.3.3.3.10 \textit{MeOH : PC ratio effect}

Generally methanol excess promotes improvement of the reaction rate and selectivity to DMC in liquid phase by shifting of the reaction equilibrium. The attempt to reduce the methanol excess of a factor of three (corresponds to the MeOH/PC ratio 6:1) to two (MeOH/PC ratio of 4:1) was done. Strong drop of PC conversion was detected – see Figure 91. Around 20 mol.% loss of the PC conversion was observed. DMC selectivity remained at the level of around 20 mol.% with slight decreased tendency at the longer TOS.

So reducing of methanol excess from 6:1 to 4:1 can be considered as a positive factor due to the keeping of DMC selectivity at the same level by using less methanol, which can be a source for some difficulties like formation of volatile dimethylether or azeotrope mixture with DMC (proportion of 6(methanol):1(DMC)). This azeotrope mixture plays an important role by reaction performing in the liquid phase. But in the vapor phase methanol proportion can be reduced without loss of DMC selectivity.

Reaction conditions: 330°C, 0.3 s contact time, 0.5-1.6 mm particle size, WHSV=1800 ml/g*h. Catalyst K-8 was used.

![Figure 91: DMC selectivity, 0.3 s contact time, 330°C](image)
3.3.3.3.11 Influence of the ionic form of Y-zeolite

Strong effect of different ionic form of Y-zeolite on the product distribution was detected. Use of Na- and Ca-form of Y-zeolite led to another products distribution that was found in case of H- and NH$_4$-form. The comparison of the reaction products is given in Table 26. It can be seen that a variety of different chemical transformations take place during the reaction. High temperatures and the presence of strong acid sites lead to many side reactions.

As it can be seen in Table 26, in case of the Ca-modified catalyst with relative small metal load of 2.4 wt.% DMC formation was still observed. But the bulk reaction mixture content was consisted from another three compounds which are presented in this Table. In case of Na-modified catalyst no DMC was formed and strong side reactions gave five main side products, which are presented in Table 26. These side products were formed with relative high selectivity, see Figure 92.

It is quite difficult to detect origin of all presented side products. The main idea to present the variety of the formed compounds and their formation selectivities was to indicate that ambient pressure and high reaction temperature don’t set an absolute limit for the high reaction selectivity. Further catalyst modification can lead to an increase of target products selectivity.

![Figure 92: Side products formation at 0.25 and 0.31 s contact time.](image-url)
Table 26: Side products formed by Y-zeolites with Na- and Ca-form

<table>
<thead>
<tr>
<th>Ionic form</th>
<th>K-11</th>
<th>K-11</th>
<th>K-13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal load in wt.%</td>
<td>6.0</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>BET in m²/g</td>
<td>722</td>
<td>722</td>
<td>394</td>
</tr>
</tbody>
</table>

--- 330°C, 0.3s contact time 330°C, 0.25s contact time 330°C, 0.3s contact time

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Compound</th>
<th>Chemical structure</th>
<th>Compound</th>
<th>Chemical structure</th>
<th>Compound</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-methoxy-propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2,2-dimethoxy-propane</td>
<td></td>
<td>2,2-dimethoxy-propane</td>
<td></td>
<td>2,2-dimethoxy-propane</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>2-propyl-1,3-Dioxolane</td>
<td></td>
<td>2-propyl-1,3-Dioxolane</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>2-methyl-3-Pentanol</td>
<td></td>
<td>2-methyl-3-Pentanol</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>3,4-dimethyl-3,4-Hexandiol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-ethyl-4-methyl-1,3-Dioxolane</td>
<td></td>
<td>2-ethyl-4-methyl-1,3-Dioxolane</td>
<td></td>
<td>2-ethyl-4-methyl-1,3-Dioxolane</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2-methylpropanoic acid, anhydride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3.3.4 Conclusions and Outlook

The presented investigations showed that the transesterification of methanol and propylene carbonate can be performed in liquid phase using homogenous catalysis conditions effectively with PC conversions up to 72 mol.%. Both dimethyl carbonate and propylene glycol can be formed with close to 100% selectivity. Oxides of alkali-earth metals can be used for these reactions. In the row BaO – SrO – CaO – MgO the activity grows except last MgO oxide. Best results can be achieved with CaO. Catalysis has a heterogeneous character but CaO particles undergo strong dispersion and cannot be effectively filtered out after reaction.

Also superbase Na/NaOH/MgO was used successfully for this reaction. Build of response surfaces allows an evaluation of the Na and NaOH concentrations influence on the PC conversion. However, the Na can be easily leached from the MgO support. This leads to the activity drop in the reusability experiments.

The following limitations of the liquid phase reactions are existing: reaching of the reaction equilibrium and difficulty in the separation of homogeneous catalyst. In order to overcome these limitations, heterogeneous catalysis was applied.

A variety of solid catalyst was tested for its suitability to catalyze methanol-propylene carbonate transesterification at ambient pressure. Relative high temperatures over 250°C were necessary to perform this reaction in vapor phase due to the high boiling point of propylene carbonate (242°C). Side effect of high reaction temperatures was destroying of the one of the reaction products – propylene glycol.

Most of the solid acids like HZSM-5 or H-BETA led to the thermo-catalytic cracking of the used propylene carbonate-methanol mixture even at relative low temperatures of 250-300°C. Thereagainst Y-zeolites showed ability to form dimethyl carbonate with the selectivity of around 25 mol.% at temperatures over 320°C. Further tuning of the reaction parameter as well of the catalyst preparation procedure allows DMC selectivity up to 45 mol.% at ambient pressure, 0.3 s contact time, VSHV of 18000 ml/g*h and 330°C. Overview on optimizations performed on reaction and catalyst parameters is shown in Table 27.

It was detected that Y-zeolites in H- and NH₄-form are suitable for PC/methanol transesterification. However, the Na- and Ca- form of the Y-zeolite lead to the strong side
product formation. Si/Al ratio of zeolite has significant effect on the amount and strength of acid sites and hence plays an important role during the reaction. Values range of 10-30 was found to be the best.

Optimal reaction temperature range of 330-340°C was found. Below 320°C very low PC conversion was detected. Above 350°C cracking reactions were prevailed and hence low DMC selectivity was observed. By increasing of the reaction temperature for 10°C from 320°C to 330°C PC conversion raises for around 20 mol.% as well as DMC selectivity grows for around 5 mol.%. Further temperature increase to 340°C lead to the same PC conversion level but a slight decrease of DMC selectivity.

Contact time plays a very important role and only its narrow range of 0.25-0.45 s (preferred 0.3-0.4 s) can be used for achieving of good DMC selectivity. Too short contact times have effect in the very low conversion. Too long contact times lead to the destruction of the hydrocarbons on the zeolite acid sites, resulting in low DMC selectivity.

VHSV has a limited influence on the reaction and at the tested values range of 10000 to 25000 ml/g*h best results were observed at VHSV’s of 15000 to 20000 ml/g*h.

Conditions of the catalyst preparation were found to be a key element for the good catalyst activity. Calcination time and temperature as well as pressing time and used pressure make conditions for future catalyst pore structure, amount and strength of the active sites. Significantly better results could be achieved after 240 min calcination time – 33 mol.% DMC selectivity against around 10-13 mol.% in case of 60 and 260 min calcination times – see Figure 88. Calcination temperature of 500°C resulted in the decreasing of the DMC selectivity. In contrast to this, catalysts, calcined at 450°C and 550°C, provided better selectivity of around 18 mol.% for both catalysts – see Figure 90.

Zeolite undergoes strong structure modifications during pressing, too. Catalyst pressing time and pressure determine not only mechanical stability of catalyst particles but also reduce its BET area and micropore volume. Especially zeolite micropores are affected by increased pressing duration and use of strong pressures. Catalysts pressed for 10 and 30 min were more active and DMC selectivity up to 45 mol.% was achieved (30 min catalyst from 160 to 250 min TOS - Figure 84). Too long pressing time resulted in the reducing of DMC selectivity
due to the destroying of micropores – around 12% micropore volume and surface loss after 2h pressing and only around 4% after 30 min. Also applied pressure has a significant influence on the catalytic activity. Catalysts pressed at 8 and 9 tons showed only limited activity and catalyst pressed at 10 tons was more active as in Figure 86 presented. Strong DMC selectivity grow up to 33 mol.% was observed in case of pressing at 10 tons.

Attempts of narrowing of particles size distribution didn’t lead to some improvements of the desired reaction characteristics. The broadest fraction 0.5-1.6 showed the best results due to the optimized gas flow in the catalyst bed.

Reducing of methanol excess from 6:1 to 4:1 was detected to be positive due to the keeping of DMC selectivity at the same level by using less methanol, which can be a source for some difficulties like formation of volatile dimethylether or azeotrope mixture with DMC (proportion of 6(methanol):1(DMC)).

Further catalyst and reaction conditions fine optimizations can lead to the better DMC and PG selectivity. The reaction goes with the decreasing of the total molecules amount, so the reaction performing at the lower pressure can also be a step to increase overall performance.

Table 27: Overview on optimized parameter in vapor phase reactions and optimal values detected

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range tested</th>
<th>Optimum/optimum range</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction temperature in °C</td>
<td>200-350</td>
<td>330-340</td>
</tr>
<tr>
<td>catalyst contact time in s</td>
<td>0,01-3</td>
<td>0,3-0,4</td>
</tr>
<tr>
<td>VHSV in ml/g(cat)*h</td>
<td>10000-25000</td>
<td>15000-20000</td>
</tr>
<tr>
<td>particle size in µm</td>
<td>400-700, 700-1000, 1000-1600, 500-1600</td>
<td>500-1600</td>
</tr>
<tr>
<td>catalyst calcination time in min</td>
<td>60-360</td>
<td>240</td>
</tr>
<tr>
<td>catalyst calcination temperature in °C</td>
<td>450-550</td>
<td>450, 550</td>
</tr>
<tr>
<td>catalyst calcination atmosphere</td>
<td>air, nitrogen</td>
<td>air, nitrogen</td>
</tr>
<tr>
<td>catalyst press time in min</td>
<td>10-120</td>
<td>30-60</td>
</tr>
<tr>
<td>catalyst press pressure in tons</td>
<td>8-10</td>
<td>10</td>
</tr>
<tr>
<td>catalyst Si/Al ratio</td>
<td>5,2-80</td>
<td>10-30</td>
</tr>
<tr>
<td>MeOH/PC molar ratio</td>
<td>4-6</td>
<td>6</td>
</tr>
<tr>
<td>Y-zeolite ionic form</td>
<td>H-, NH₄-, Na-, Ca-</td>
<td>H-, NH₄-</td>
</tr>
</tbody>
</table>
4 Summary and Outlook

Some applied aspects of the ethyl benzene to the styrene reaction in the riser reactor were studied. Unusual strong carbon dioxide formation during the reaction was explained through the oxygen in the catalysts pores and its sequent oxidation during the reaction. Use of only nitrogen as a feed in a blank experiment as well as argon flushing of the catalyst prior to the experiments didn’t lead to the reducing of the oxygen content in the product mixture. High reaction temperature and long gas residence times favor the increased by products formation. Positive effect of the water presence in the feed was observed. A 30% less CO₂ was formed at 1 s GRT and 700°C if 30 mol.% water was added to the feed.

Another point of this work consisted in the investigations of the Mo/HZSM-5 catalysts use for the methane dehydroaromatization. Several reaction optimizations like WHSV level, reaction temperature, carbon dioxide addition were performed in the fixed bed reactor at ambient pressure. The methane WHSV level was found to be optimal in the range of 1.5-2.0 h⁻¹. Further WHSV increasing leads to the activity drop in terms of mmol produced aromatic per gram catalyst per hour. Increasing of the temperature favors the desired aromatic formation but causes strong irreversible catalyst deactivation. Temperature optimum lies in the range 700-725°C. Detrimental effect of the carbon dioxide addition was detected. Methane conversion as well as aromatic formation were significantly suppressed by addition of 3% CO₂ to the methane feed.

Moreover use of the fluidized bed reactor at ambient pressure was studied. Around 15 % more aromatic yield compare to the fixed bed reactor were achieved in the fluidized bed reactor. However, catalyst underwent strong deactivation already after several hours at the fluidized conditions. The reasons for the deactivation were investigated. Significant loss of crystalline structure and molybdenum leaching were detected. Strong reducing of the particles size distribution was observed also. Mechanical stability of the particles has to be improved to use this catalyst in fluidized bed reactor.

Furthermore, the production of the “green” reagent dimethyl carbonate was investigated in this work. Catalyst screening for the reaction performing in the liquid phase was done. CaO showed best results as well as superbase MgO/Na/NaOH. PC conversion of around 70 mol.% with 99 mol.% DMC and PG selectivity was achieved.
However, reaction performing in the liquid phase doesn’t allow effective reuse of the catalyst. For this reason it was attempted to perform this reaction heterogeneously in fixed bed reactor in the vapor phase and at ambient pressure. Catalyst screening was done. Y-zeolites showed highest activity and were able to achieve up to 25 mol.% DMC selectivity at around 60 mol.% PC conversion during initial experiments. An optimization of the reaction conditions as well of the catalyst preparation method led to the grow of DMC selectivity up to 45 mol.% at around 60 mol.% PC conversion. Overview on optimized parameters is given in Table 27. Many parameters have a strong influence on the DMC selectivity and only its narrow values range can be used for the effective reaction performance. Further selectivity increase cannot be ruled out. It was detected that H- and NH₄-form of Y-zeolites are suitable for PC/methanol transesterification. In contrast to this Na- and Ca- form lead to the strong side products formation.
5 Experimental

5.1 Reactors set up and methodology

5.1.1 Liquid phase stirring reactor – DMC Production

The required amount of propylene carbonate and methanol as well as stirring element was placed inside a 50 ml flask. Afterwards a defined catalyst amount was added. Finally the system was placed inside an oil bath (this was defined as the reaction start) to bring the mixture to the intended reaction temperature. Stirring speed was maintained at 800 rpm. The catalysts activity was not limited by stirring speed (maximum of PC conversion was arrived within few seconds/minutes), so this parameter was not varied. The samples were taken by a long syringe. Mesitylene was used as an external standard. Products were analyzed on a 60 m FE-SE54 column (70°C to 270°C, at 8°C/min, 10 min isotherm at 270°C).

5.1.2 Fixed bed reactor for MDA

The reactor was a quartz tubular reactor (3.5 mm i.d.). Prior to the experiments, the reactor had been immersed in KOH for cleaning, followed by washing with water and acetone, before drying at 130°C under air. Approximately 1.0 gram of fresh catalyst was placed inside a tubular quartz reactor. The ratio of the catalyst bed length to the bed diameter was around 40. The fixed bed reactor process flow and instrumentation diagram is shown in the Figure 93. The required gases entered the quartz tube reactor via mass flow controllers. The oven was heated by heaters controlled by temperature regulator Eurotherm 91e. Smooth heat distribution within the oven was provided by a rotating fan at the bottom of the oven. After reaction the products were cooled down and collected in an iso-propanol / CO$_2$ cooling trap. Dichloromethane was used as a solvent to dissolve solid naphthalene crystals formed prior to the cooling trap. Mesitylene was used as an external standard. Products were analyzed on a 60 m FE-SE54 column (70°C to 270°C, at 8°C/min, 10 min isotherm at 270°C).

The following procedure describes one cycle of the experiment:

- Catalyst heated to 580°C under air (3°C/min and ~1.5 Nl/h).
- System maintained under air flow at 580°C for 15 hours.
System flushed with nitrogen for 30 minutes (~1.5 nL/h).
Switched to CH$_4$ and heated to 700°C (3°C/min and ~1.5 nL/h).
System maintained at 700°C for the intended reaction duration.
Switched to argon and cooled to room temperature (3°C/min and ~1.5 nL/h).

The start of the time on stream is defined as the time when which the reaction temperature reached 700°C.

![Diagram](image)

**Figure 93: Process flow and instrumentation diagram of the MDA fixed bed reactor system**

### 5.1.3 Fixed bed reactor for DMC production

Reactor was a steel spiral reactor (5 mm i.d.). Approximately 2.0 gram of fresh catalyst was placed inside the reactor. The ratio of the catalyst bed length to the bed diameter was around 12. The fixed bed reactor piping flow and instrumentation diagram is represented in the Figure 94. The required gas flow was controlled by rotameter and the liquid educts were pumped by Latek micropump. The oven was heated by heaters which were controlled by Eurotherm 91e temperature regulator. Smooth heat distribution within the oven was provided by a rotating fan at the bottom of the oven. After reaction the products from the reactor were cooled down and collected in an iso-propanol / CO$_2$ cooling trap. Acetone was used as a solvent to dissolve the reaction products. Mesitylene was used as an external standard. Products were analyzed on a 60 m FE-SE54 column (70°C to 270°C, at 8°C/min, 10 min isotherm at 270°C).

The following procedure describes one cycle of the experiment:
• Catalyst heated to 300°C under nitrogen
• System maintained under nitrogen flow at 300°C for 2 hours
• System was brought to the required temperature under nitrogen flow
• The pump was switched on to bring the PC/methanol mixture at needed nitrogen flow to the reactor
• Samples were taken after defined times on stream, system maintained for intended reaction duration
• The pump was switched off and the system was cooled down

The start of the time on stream is defined as the time when the Latek pump was switched on. Figure 77 represents the fixed bed reactor set up.

![Diagram of fixed bed reactor for propylene carbonate/methanol transesterification](image)

**Figure 94: P&I diagram of fixed bed reactor for propylene carbonate/methanol transesterification**
5.1.4 Fluidized bed reactor for MDA

A quartz fluidized bed reactor was used for the investigations of MDA. A process and instrumentation diagram (P&ID) of the entire system is presented in Figure 96. During the reaction the typical temperature in the reactor was 973 K, in the cyclone 673 K, in the tube after cyclone 593 K to avoid deposition of naphthalene ($T_{\text{boil}} = 491$ K) in the pipe. The reactor has double layer insulation to keep safely high temperatures up to 800°C during the reaction.

Four temperature controllers Eurotherm 818, one for each described below heating zone, regulated the temperature during the reaction:

- preheater,
- reactor,
- separator (cyclone),
- tube for reaction products.

The gas flow was regulated by mass flow controllers of Brooks (type 5850E). The gas mixture was added to the system through preheater and enters the fluidized bed reactor through the filter at needed reaction temperature. The gas mixture contacts the fluidized
catalyst bed. After that the solid-gas mixture enters the cyclone where the solid particles are separated from the gas phase. The solid catalyst particles fall down back to the reactor. The reaction mixture in the gas phase is conducted via a tube to the cooling trap.

Prior to the reactions the pressure drop over the glass filter inside the reactor at temperatures of 293 K and 973 K was determined. Subsequently the MFV (Minimal Fluidization Velocity) was determined for the catalyst bed. The approach of the $\Delta P$ measurements according to the gas velocity was applied. An example of measured MVF is represented in Figure 97. Measured values corresponded well with the ideal curve, which is shown for comparison. The reactions were carried out at the gas velocities larger than MFV approx. a factor of 1.5. This makes sure that the catalyst bed is in the fluidized state.

The following procedure describes one cycle of experiment.

- Catalyst heated to 580°C under air (5°C/min and ~15 Nl/h).
- System maintained at 580°C under air for 12 hours.
- System flushed with nitrogen for 30 min (~15 Nl/h).
- Switched to CH$_4$ and heated to 700°C (5°C/min and ~60 Nl/h).
- System maintained at 700°C for intended reaction duration.
- Switched to nitrogen and cooled to room temperature (5°C/min and ~15 Nl/h).

The start of the time on stream is defined as the time when the reactor reached required reaction temperature.

Figure 98 represents a picture of the fluidized bed reactor set up.
Figure 96: Process flow and instrumentation diagram of the fluidized bed reactor system

Figure 97: An example of detected MFV and ideal curve
5.1.5 Riser reactor for Ethyl Benzene to Styrene

A quartz glass riser reactor was used for the investigations of styrene production. It consists out of five main zones as shown in Figure 99 and in the reactor picture Figure 100: pre-heater in form of a coil, reactor, hopper for fresh catalyst, cyclone and product recovery vessel.

A Brooks mass flow controller of type 5850E regulates ethane flow. Together with the ethyl benzene, which is pumped into this pre-heater zone at about half-length as a liquid with a Latek pump, they are heated to the desired temperature. This temperature is controlled by a thermocouple just underneath a quartz glass filter (< 80 µm). This filter prevents the catalyst falling into the pre-heater. The thermocouple is situated inside a glass ‘finger’ for its better determination and control of the temperature the gas flow. The thermocouples are not in
Experimental – Reactors set up and methodology

direct contact with ethane, ethyl benzene and catalyst because there are no gas tight seals at 600°C. Furthermore the metal of the thermocouple would cause side reactions.

The fresh catalyst is stored in a hopper, equipped with baffles to ensure a good catalyst down flow, in which the catalyst can be heated. During the reaction the catalyst flows down in hopper under its own weight and enters the reactor just above the quartz glass filter. An additional “anti-arching” nitrogen flow was used in order to prevent blocking of catalyst particles at the entrance to the riser. Without this “anti-arching” nitrogen flow it was possible that catalyst blocked the tube at the low gas stream or the catalyst flow was unstable (pulsing). The riser reactor ends in a cyclone, in which the catalyst is separated from the product flow. The catalyst drops into a recovery vessel, from which it can be taken to be regenerated batch wise. The organic products are cooled down in a double walled recovery vessel (cooled with a cryostat filled with iso-propanol at ca. -10°C); gas samples of the off-gas can be taken with a gas mouse.

The following procedure has been carried out during one cycle of experimentation:

- The apparatus was heated under flowing $N_2$ with 5°C/min to the following temperatures: $T_{\text{pre-heater}} = 400°C$, $T_{\text{reactor}} = 500°C$, $T_{\text{hopper}} = 500°C$, $T_{\text{bottom cone hopper}} = 500°C$,
- Afterwards the catalyst recovery vessel and the fresh catalyst hopper were flushed with argon. The calcined catalyst, stored under argon, was filled into the hopper under flowing argon. Subsequently, the hopper temperature was increased to 650°C and the reactor temperature to 550°C. The system was left to stabilize at these temperatures overnight,
- The relative low temperature of pre-heater zone of 400°C was chosen to avoid the thermal cracking of ethyl benzene,
- For the reaction itself the ethane flow and the ‘anti arching’ nitrogen flow were started until a rising system was obtained. Then the ethyl benzene flow was started. This was defined as $t = 0$ min. During the reaction the catalyst flow was monitored continuously to ensure that indeed a rising system was obtained. This monitoring was done visually by observing the catalyst falls down in the recovery vessel,
- With a gas mouse gas samples were taken after 30 min TOS, which should ensure a stable system,
- After all catalyst was used the ethyl benzene and ethane flows were stopped, and the reactor was flushed with nitrogen for several minutes,
- The product recovery vessel, which was cooled to ca. –10°C during the reaction, was taken from the reactor, and washed with ethanol. This solution was analyzed by gas chromatography,
- The catalyst throughput was determined by weighing the empty catalyst recovery vessel before and after the reaction,
- Between the reactions the catalyst remaining in the reactor was removed with a vacuum cleaner.

Figure 99: Riser reactor set up
5.2 Chemicals and Gases

Most of the solid, fluid and gaseous materials were ordered by Aldrich, Merck or Fluka catalogues in synthesis quality and were applied without further purification.
5.3 Catalysts

DOW Chemicals kindly provided catalyst for dehydrogenation of ethyl benzene. The catalyst was calcined in batches under air by heating with 5°C/min to 120°C, which temperature is maintained for 3 h. Subsequently, the catalyst was heated to 650°C over 300 min, kept at 650°C for 5 h, and cooled down to 200°C. At this temperature the calcined catalyst was transferred into glass bottles, in which it is stored under argon and left to cool down to the ambient temperature.

4% Mo/HZSM-5 zeolite for methane dehydroaromatization was kindly provided by ENICHEM Company. Physical mixtures of Mo₂C and HZSM-5 and MoO₃ and HZSM-5 were prepared by mixing of corresponded amount of components.

Different zeolites for DMC production came from BASF, Zeolyst, USY, Valfor, Wessalith or PQ companies. Table 28 represents Y-zeolites which were used as a starting material for the preparation of different catalysts for the PC/methanol transesterification. CaO was prepared from CaCO₃ by keeping it in air atmosphere at 600°C during 4h. Other metal oxides were purchased in Aldrich catalogue and were used without any pre-treatments.

Table 28: List of supports used, their ionic form and origin

<table>
<thead>
<tr>
<th>Internal name</th>
<th>Name</th>
<th>SiO₂/Al₂O₃</th>
<th>Ionic Form</th>
<th>Origin, Fa.</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV 00/08</td>
<td>CBV 780</td>
<td>80</td>
<td>H</td>
<td>Zeolyst</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 92/71</td>
<td>CBV 400</td>
<td>5.2</td>
<td>H</td>
<td>Zeolyst</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 97/02</td>
<td>-</td>
<td>5.6</td>
<td>Na</td>
<td>Wessalith NaY</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 94/50</td>
<td>CBV 720</td>
<td>30</td>
<td>H</td>
<td>SDUS PQ</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 94/46</td>
<td>CBV 760</td>
<td>55</td>
<td>H</td>
<td>Valfor</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 94/45</td>
<td>CBV 740</td>
<td>42</td>
<td>H</td>
<td>Valfor</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 94/44</td>
<td>CBV 712</td>
<td>11.5</td>
<td>NH₄</td>
<td>Valfor</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 94/11</td>
<td>-</td>
<td>-</td>
<td>Ca</td>
<td>001/KH</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 93/17</td>
<td>-</td>
<td>6</td>
<td>H</td>
<td>USY</td>
<td>FAU</td>
</tr>
<tr>
<td>HV 92/72</td>
<td>CBV 500</td>
<td>5.2</td>
<td>NH₄</td>
<td>Zeolyst</td>
<td>FAU</td>
</tr>
</tbody>
</table>
Table 29: List of used catalysts and catalyst preparation

<table>
<thead>
<tr>
<th>Catalyst, internal name</th>
<th>Support/internal name</th>
<th>$\text{SiO}_2/\text{Al}_2\text{O}_3$</th>
<th>Ionic form</th>
<th>Surface area of fresh material in $\text{m}^2/\text{g}$</th>
<th>Structure</th>
<th>Calcination</th>
<th>Press in tons</th>
<th>Press time in min</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-6 CBV 400</td>
<td>H</td>
<td>5.2</td>
<td>H</td>
<td>730</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-8 CBV 712</td>
<td>NH$_4$</td>
<td>11.5</td>
<td>H</td>
<td>730</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-9 CBV 720</td>
<td>H</td>
<td>30</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-10 CBV 740</td>
<td>H</td>
<td>42</td>
<td>H</td>
<td>740</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-11 HV 97/02</td>
<td>Na</td>
<td>5.6</td>
<td>H</td>
<td>722</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-12 CBV 760</td>
<td>H</td>
<td>55</td>
<td>H</td>
<td>720</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-13 HV 94/11</td>
<td>-</td>
<td>Ca</td>
<td>394</td>
<td>FAU</td>
<td></td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-14 HV 93/17</td>
<td>H</td>
<td>6</td>
<td>H</td>
<td>595</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-15 CBV 500 HV 92/72</td>
<td>NH$_4$</td>
<td>5.2</td>
<td>H</td>
<td>750</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-16 CBV 720 HV 94/50</td>
<td>H</td>
<td>30</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-17 CBV 720 HV 94/50</td>
<td>H</td>
<td>30</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 6h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-18 K-9 Batch 2</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 500°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-19 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 450°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-20 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 550°C</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>K-21 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 1h at 500°C</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>K-22 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 550°C</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>K-23 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 6h at 500°C</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>K-24 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 550°C</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>K-25 CBV 720 HV 94/50</td>
<td>30</td>
<td>H</td>
<td>H</td>
<td>780</td>
<td>FAU</td>
<td>Air calcination 4h at 550°C</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Superbase MgO/Na/NaOH for DMC production was prepared as follows:
Required amount of MgO was placed inside a metal stirring reactor. The reactor was flushed
with nitrogen during all preparation procedure. The reactor was heated to 350°C with heating
rate of 5°C/min. Then it was maintained at 350°C for 3h. After that NaOH was added and
maintained next 3h at 350°C. Afterwards Na was added. After stirring for the next 2h at
350°C the reactor was cooled down at 5°C/min ramp and finally the prepared catalyst was
transferred to the sealed flask.
Hydrotalcites for DMC production were produced on the following way:
First Mg$_2$Al-NO$_3$ was prepared by adoption of the induced hydrolysis method developed by Taylor [140]. Dissolved CO$_2$ was removed by bubbling N$_2$ through deionized water. This solution was added drop wise to an aqueous solution of NaOH (375 mmol in 100 ml) in 90 min, with continuous stirring. The pH of the mixture was 13. Following the addition, the mixture was kept at 346K for 18h by continuous stirring. The resultant slurry was cooled down to the room temperature and solid product was separated by filtration, washed with deionized water and dried at 393 K overnight.

Then Mg$_2$AlOH was prepared by ion-exchange of Mg$_2$AlNO$_3$. Mg$_2$AlNO$_3$ (1g) was added to a NaOH solution in 100 ml deionized water. The NaOH was taken in 50-100% stoichiometric excess of NO$_3^-$ amount in Mg$_2$AlNO$_3$. The mixture was stirred for 2h at 343K. After two ion-exchange treatments the product was separated by filtration, washed and dried at 393K overnight.

5.4 Product analysis

5.4.1 Gas chromatography

The fluid reaction products were cooled and collected in an iso-propanol / CO$_2$ cooling trap. Dichloromethane or acetone was used as a solvent to dissolve reaction products (solid naphthalene crystals formed prior to the cooling trap in case of MDA reaction). Mesitylene was used as an external standard. Products were analyzed on a 60 m FE-SE54 column (70°C to 270°C, at 8°C/min, 10 min isotherm at 270°C).

5.4.2 Mass spectrometry (GC-MS)

Mass spectrometry was used for identification of unknown products. Follow apparatus and conditions were used:
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Varian 3400CX</td>
</tr>
<tr>
<td>MS</td>
<td>Varian Saturn 3</td>
</tr>
<tr>
<td>Data processing</td>
<td>Varian Saturn, Vers. 5.2</td>
</tr>
<tr>
<td>Energy</td>
<td>70 eV</td>
</tr>
<tr>
<td>Ionization</td>
<td>Electron ionization</td>
</tr>
<tr>
<td>Column</td>
<td>25 mSE 54</td>
</tr>
<tr>
<td>Column temperature</td>
<td>50 – 270°C</td>
</tr>
<tr>
<td></td>
<td>6 min isotherm 50°C</td>
</tr>
<tr>
<td></td>
<td>10°C/min</td>
</tr>
<tr>
<td>Evaporator temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He, 1 bar pressure</td>
</tr>
</tbody>
</table>

### 5.4.3 ICP-AES elementary analysis

For detection of metal load in the catalysts Spekstro-Flamme D-apparatus of Spectro company was used. The samples were dried during 24 h at 120°C. Then they were solved in the mixture of 750ml 25% H\textsubscript{2}SO\textsubscript{4}, 15 ml distilled water and 150 ml HF (40%). In few cases ultrasound bath was used to solve samples.

### 5.4.4 Thermogravimetric analysis

Thermogravimetric analysis was done on STA 409C apparatus of Netzsch 209/2/E at follow conditions: temperature range 20-1000°C, heating rate 2 °C/min, air atmosphere. TG, DTA and DSC were resulted.

The peaks of the mass loss processes were detected graphically on the DSC diagram basis.

### 5.4.5 CO\textsubscript{2} Temperature Programmed Desorption (CO\textsubscript{2}-TPD)

CO\textsubscript{2}-TPD was done for the measurements of catalysts basicity. This was done on Porotec TPD RO 1100 apparatus. The sample was flushed with nitrogen for 2h at 300K, and then it was loaded by CO\textsubscript{2} at 80°C during 2h. Afterwards it was heated to 600°C at 10°C/min ramp. Desorpted CO\textsubscript{2} was detected on TCD detector.
5.4.6 BET analysis

Surface area, micropore area and volume of the catalyst were measured by BET method on ASAP 2000 of Micromeritics.

5.4.7 X-ray diffraction analysis (XRD)

X-ray diffraction (XRD) patterns were obtained in air on the Siemens D5000 apparatus.
# Annex 1. Boiling points and danger classes of used chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Boiling point in °C</th>
<th>Danger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Carbonate (PC)</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Propylenglycol (PG)</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>Azeotrope DMC*6MeOH (30 wt.% DMC, 70 wt.% MeOH)</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>Mesitylene</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>145</td>
<td></td>
</tr>
</tbody>
</table>
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