Methods for the Synthesis of Linear Dialkylaromatic Compounds by the Use of Heterogeneous Catalysts

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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Upon completion of this work, I would like to express my deepest gratitude towards my Thesis Director, Professor Hölderich. He allowed me to undertake my researches in a high quality laboratory and never hesitated in putting trust in me.

I would also like to acknowledge the work of Prof. Dr.-Ing. Th. Melin who kindly took over the responsibility of the second reviewer.

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À Young Wook et à Charles
## CONTENTS

### A. INTRODUCTION

### B. PRIOR ART

#### 1. DEHYDROGENATION

1.1. THERMODYNAMIC

1.2. REACTION CONDITIONS

1.3. CATALYSTS

1.4. DEHYDROGENATION TO AROMATIC OR HETEROAROMATIC COMPOUNDS

1.5. DEHYDROGENATION OF ALCOHOLS TO ALDEHYDES OR KETONES

#### 2. ALKYLATION

2.1. THERMODYNAMIC

2.2. REACTION CONDITIONS AND CATALYSTS

2.3. MECHANISM

2.4. SHAPE SELECTIVITY

2.5. ALKYLATION OF BIPHENYL AND NAPHTHALENE WITH PROPYLENE

#### 3. ULLMANN COUPLING

3.1. CLASSICAL ULLMANN COUPLING

3.2. MODIFIED ULLMANN COUPLING

3.3. CATALYTIC ALTERNATIVE

### C. RESULTS AND DISCUSSION

#### 1. DEHYDROGENATION OF PINENES TO p-CYMENE

1.1. α-PINENE VERSUS α-LIMONENE OVER SILICA BASED CATALYSTS

1.2. ROLE OF ACIDITY

1.3. ACID CRACKING VERSUS HYDROGENOLYSIS

1.4. REACTION MECHANISM

1.5. ROLE OF HYDROGEN AND DEACTIVATION

1.6. CRUDE SULFATE TURPENTINE AS REACTANT

1.7. CONCLUSION

#### 2. ALKYLATION OF BIPHENYL AND NAPHTHALENE
## CONTENTS

- **2.1. Activity of Standard Materials** 53
- **2.2. Modifications Brought to Zeolite Beta** 55
- **2.3. Dealumination by Acid Leaching** 56
- **2.4. Influence of the Temperature** 59
- **2.5. Catalytic Activity, Deactivation and Coke Formation** 60
- **2.7. Structural Aspects of Zeolite Beta** 66
- **2.8. Characterization with Nitrogen Adsorption, XRD and SEM** 67
- **2.9. Characterization by FTIR Spectroscopy** 69
- **2.10. Characterization by $^{29}$Si MAS NMR and $^{27}$Al MAS NMR** 73
- **2.11. Discussion about Shape Selectivity in Zeolite Beta** 79
- **2.12. Conclusion** 81
- **3. Catalytic and Non-Catalytic Coupling of p-Chlorotoluene** 83
  - **3.1. The Catalytic Coupling with Chlorine as Product** 83
  - **3.2. The Non-Catalytic Coupling** 84
  - **3.3. The Catalytic Coupling with a Reducing Agent** 91
  - **3.4. Is the Catalytic Reaction Structure Sensitive?** 98
  - **3.5. Conclusion** 101
- **D. General Conclusion** 103
- **E. Experimental Procedure** 105
  - **1. Catalysts Preparation** 105
  - **2. Reaction Conditions** 107
  - **3. Chromatography and Mass Spectroscopy** 108
  - **4. Characterization by BET, ICP, TG, XRD, SEM, and TEM** 109
  - **5. Characterization by TPD, TPO and CO Chemisorption** 110
  - **6. Characterization by FTIR** 111
  - **7. Characterization by MAS NMR** 112
- **F. References** 114
A. INTRODUCTION

The department of Chemical Technology and Heterogeneous Catalysis is specialized in the application of heterogeneous catalysis in the field of fine chemistry and specialty chemicals. One of its objectives is to improve existing chemical processes by employing heterogeneous catalysts. Most of the processes in fine chemistry are still based on homogeneous catalysis with inherent major drawbacks. These drawbacks are, among others, complicated separation of reactant and catalyst, corrosion, production of large quantities of by-products such as salts, and trouble with waste disposal. Accordingly, these problems have brought a general awareness for environmental benign processes and the concept of “green chemistry” has nowadays become popular. The benefits are that a number of old traditional processes have already been replaced by environmentally friendly ones and a large number of new processes are currently under development [1].

A second approach of the department is to develop new catalytic routes for the synthesis of high added value chemicals. Such kind of work is of course risky and associated with low chances of commercial success. Nevertheless it brings a new insight on catalytic chemistry and opens the ways for new chemical laboratory synthesis. Finally a third approach, which is in close relation with the second one, is to develop processes that are not based on typical petrochemical feedstock. Then, the use of renewable materials such as cellulose, raps oil or terpenes is of major interest [2-4].

Dialkylaromatic compounds are important intermediates for thermoplastic polyesters and liquid crystal polymers [Scheme 1] [5]. Poly(ethylene terephthalate) (PET) is a common material with its main application devoted for carbonated beverages and mineral water containers as well as for fibers and films. Its production starts from the cheaply available p-xylene (1) that is oxidized to the corresponding terephthalate acid (2). The acid is afterwards transesterificated with ethylene glycol and polymerized to PET. The transesterification can be also performed with butane-1,4-diol to give in the next polymerization step poly(1,4-butylene terephthalate) (PBT), a fiber with superior properties. However, for advance fibers and films with superior strength and for high performance liquid crystalline polymers the use of mononuclear aromatic compounds is unsuitable and the practice must turn its attention to binuclear aromatic compounds.
Binuclear alkylaromatic compounds such as those depicted in Scheme 1 are the most promising candidates for fibers and films of high quality. These aromatic compounds are 2,6-dimethylnaphthalene (2,6-DMN), 2,6-diisopropylnaphthalene (2,6-DIPN), 4,4’-dimethylbiphenyl (4,4’-DMB), and 4,4’-diisopropylbiphenyl (4,4’-DIPB). The presence of an isopropyl group instead of a methyl group is not of great concern. They must be oxidized to their dicarboxylic acid counterparts (3) and (5). The oxidation principle is the same as for m-xylene. The combination of naphthalene-2,6-dicarboxylic acid with ethylene glycol gives obviously poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and a combination with butane-1,4-diol gives poly(1,4-butylene naphthalene-2,6-dicarboxylate) (PBN). Only two

![Scheme 1: molecular structure of the compounds under investigation](image_url)
companies are now producing PEN and PBN namely Amoco and Mitsubishi Gas Chemical. Commercial products with a biphenyl structure are so far not employed commercially and cheap synthetic method for the starting material must still be found.

Liquid crystal polymers (LCP) are different from the above mentioned compounds in such a way that their building monomers must all be of aromatic nature. This is the reason why they are expensive and used only as engineering plastic. For example, VECTRA from Hoechst is a copolyester of 6-hydroxy-2-naphthoic acid (4) with 4-hydroxybenzoic acid. This material has a unique combination of high thermal stability and outstanding chemical and solvent resistance. The development of affordable monomers with a biphenyl structure (6) is of prime importance for the development of specialized materials such as biomedical devices and printed circuit boards.

p-Cymene (7) could, as it is the case with 2,6-DIPN or 4,4’DIPB, be oxidized to its corresponding acid (terephthalate acid (2)). It is however more expensive than p-xylene and not used for this purpose. p-Cymene is nevertheless an important product and valuable intermediate in the chemical industry. Among others, it is used as a solvent for dyes and varnishes, as a heat transfer medium, as an additive in fragrances and musk perfumes and as a masking odor for industrial products. The main use of p-cymene is however its transformation to p-cresol (8) which in turn can be alkylated to the widely used antioxidant 2,6-di-tert-butyl-p-cresol (9).

The objective of this work is to find out new heterogeneous catalysts for the production of linear alkylaromatic compounds. Three types of reactions will be investigated. The first reaction is concerned with the dehydrogenation of naturally occurring terpenes to the more commercially valuable p-cymene. The second reaction deals with the alkylation of biphenyl and naphthalene with propylene to synthesized shape selectively 4,4’-DIPB and 2,6-DIPN. Finally, the third reaction will explore the possibility to turn the classical Ullmann reaction catalytic and couples two p-chlorotoluene into 4,4’-DMB.

The work will be divided in the following manner. Chapter A is the current introduction. Chapter B will present a literature review of the three different types of catalytic reaction namely dehydrogenation, alkylation and Ullmann coupling. The review will be focused in a first part on general aspects of each type of reaction followed by concrete examples relevant
for this work. Within this review, the aspect of fine chemistry will be highlighted. The third chapter (chapter C) will present the whole experimental results with a proper discussion on each subject. It will be divided in three main sections, since the three subjects are quite different in their catalytic aspects. A general conclusion for the three subjects will be given in chapter D. Finally, the experimental section (chapter E) is included at the end of the work and the bibliography closes the dissertation (chapter F).
B. PRIOR ART

1. DEHYDROGENATION

Dehydrogenation is a key reaction in the production of commodity chemicals such as butadiene, styrene and formaldehyde and in the catalytic reforming of petroleum naphtha [6-8]. In the fine chemical industry, however, dehydrogenation is used less than the numerous hydrogenation reactions which are available. Dehydrogenation is usually an endothermic reaction which requires high temperatures. For such conditions the chemical stability of many fine chemicals is often insufficient. Most of the dehydrogenation reactions used in fine chemistry yield aromatic or heteroaromatic compounds and aldehydes or ketones.

1.1. Thermodynamic

The dehydrogenation of organic molecules producing molecular hydrogen can be classified into different families of reactions. The dehydrogenation may form isolated double bonds, aromatic compounds, heteroaromatic compounds, aldehydes, or ketones. In all these reactions the product yield is limited by thermodynamics. Figure 1 shows the thermodynamic equilibrium attained for different dehydrogenation reactions. It is illustrated that the formation of isolated double bonds requires a higher temperature even though the enthalpy of reaction is lower than for aromatic compounds. The aromatic stability and the high entropy gain resulting from the loss of three hydrogen molecules are the reasons for the formation of aromatic compounds in a narrow range of lower temperatures (200-300°C). In comparison, the dehydrogenation of secondary alcohols to ketones occurs over a wider range of temperatures. The presence of substituted groups (alkyl, aryl) attached to the aromatic ring further favors the formation of aromatic compounds at lower temperatures.

The use of hydrogen acceptors enables reactions of unstable molecules at lower temperatures. Examples of hydrogen acceptors are sulfur or selenium [9], α-olefins [10], dimethyl maleate [11], diethyl maleate or fumarate [12], and chloranil [13].
1.2. Reaction conditions

Reaction conditions for the dehydrogenation of single saturated bonds to isolated double bonds are severe. High temperatures (> 500°C) and low pressures (<= 1 bar) are essential if reasonable conversions are to be achieved. Under such conditions coke is formed in a matter of minutes and regeneration via oxidation is a process combined with the dehydrogenation. The thermal stability of the catalyst is, therefore, of major concern. Noble metal carriers such as alumina are preferred because of their improved sintering stability when compared with silica. Alumina induces a good metal support interaction (MSI) especially when the metal has an oxidation state of 2+ under oxidizing conditions.

The presence of hydrogen is usually not detrimental when aromatic compounds are formed. It has even been reported to be a promoter [14]. The benefit of using hydrogen is probably related to the better desorption rate of the aromatic molecule. It has been suggested that this desorption step is the rate limiting factor [15]. Hydrogen also prevents rapid accumulation of carbon on the metal surface. Figure 1 shows that the introduction of hydrogen slightly
increases the optimum temperature for high-equilibrium conversions, as shown for the dehydrogenation of cyclohexane to benzene. Dehydrogenation at higher temperatures also means a faster reaction rate and a higher space-time yield.

The dehydrogenation can also be performed in the liquid phase, when lower temperatures are required. High pressure of an inert gas is sometimes required to maintain the reactants in the liquid state. The hydrogen gas evolving from the reaction can be stripped out of the reaction mixture by means of circulating an inert gas such as nitrogen. The constraints imposed by the equilibrium conversion are thereby reduced. Small amounts of oxygen can also be added to react slowly with the hydrogen formed [16].

Gas phase reactions are usually performed with a series of fixed bed adiabatic reactors with re-heating between each catalytic bed. Liquid phase reactions are usually performed in a slurry reactor with a circulating inert gas. The new trends in dehydrogenation reactors and conditions are membrane reactors [17], wall reactors [18], reactions performed in supercritical water [19] and oxidative dehydrogenation [16].

1.3. Catalysts

Hydrogenation/dehydrogenation reactions are reversible processes. Hence, a catalyst, which is good for hydrogenation, is also suitable for dehydrogenation. Problems arise because dehydrogenation is performed at higher temperatures. Indeed, it is more difficult to favor the cleavage of the C-H bond over the cleavage of the C-C bond at high temperatures and hydrogenolysis is usually followed by carbonization and coke formation as side reactions.

Catalysts for dehydrogenation are either metallic, oxidic or basic. Metallic catalysts based on Pd and Pt are usually used for the dehydrogenation of cyclic compounds to aromatic compounds. The dehydrogenation of alcohols to aldehydes or ketones is usually performed on oxides such as ZnO, CuO, Cr₂O₃ and Fe₂O₃, because the OH group of an alcohol can undergo an ionic interaction with an oxidic material. This interaction has a significant influence on selectivity. Each type of catalyst is now discussed in more detail:
1. Metallic catalysts are usually based on Pt and Pd because these metals have by far the lowest hydrogenolysis activity from group VIII metals while sustaining good hydrogenation/dehydrogenation activity [15]. The cleavage of C-H, O-H, and H-H bonds is, moreover, usually regarded as structure insensitive whereas the cleavage of C-C bonds requires a large ensemble of metal atoms and is therefore considered structure sensitive. Thus, the dilution of a noble metal with a group IB metal is one of the most efficient means of reducing hydrogenolysis. The effect can be interpreted in terms of a geometric or an electronic factor. The geometric factor supposes that the large ensembles of atoms are heterogenized because of an alloying effect. The electronic effect supposes that different metal-adsorbate bond strengths are modified so that hydrogenolysis is significantly reduced. The alloying effect is not only limited to group IB metals. It is, for example, common to alloy Pt with Ge, In, Ga and Sn. The dehydrogenation activity of Pd is increased when alloyed with Ni, Ru and Pt. Sulfidation of Ni is another method of using a good hydrogenation catalyst for dehydrogenation.

2. The most active oxides for dehydrogenation under reductive conditions are usually metal oxides such as Fe₂O₃ and metal oxides of group VIA (Cr, Mo, W). They have a variable oxidation state and can be supported on high surface-area carriers. Cr₂O₃ is used as such or supported on γ- or θ-alumina, or ZrO₂. The latter support has intrinsically lower acidity than alumina. When alumina is used, an alkali or a rare earth metal is necessary to suppress the acidity and to avoid dehydration. CuO, ZnO, Cr₂O₃, Fe₂O₃ and a combination thereof are frequently used for the dehydrogenation of alcohols. Cu, which can also be employed as a metal, is prepared in high percentage by co-precipitation with another metal as in Cu-chromite. The resulting material has better stability against sintering. This is also true for Zn and when combined with Cr or Fe forms a spinel which has a large surface area.

3. Purely basic oxide catalysts have, to some extent, a dehydrogenation function. An example is CaO in the dehydrocyclodimerization of conjugated dienes [20]. Hattori has published a review on the multi-functionality of basic catalysts in the fine chemistry [21].

The next sections will discuss in more detail different dehydrogenation reactions performed in organic synthesis (see Table 1 for a summary). The reactions have been chosen to exemplify the complex reaction conditions and catalyst formulation associated with different reactants.
Table 1: selected dehydrogenation reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction schemes</th>
<th>Conditions</th>
<th>Catalysts</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>Dehydrogenation to aromatic or heteroaromatic compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td><img src="image1.png" alt="Chemical Structures" /></td>
<td>a) $T \approx 300^\circ C$, $P_{H_2} = 1$ bar, $H_2$/terpenes $= 3$, WHSV $= 3$ for Pd/SiO$_2$; b) reactive distillation, $T = 140^\circ C$, $P &lt; 0.01$ bar, triethylamine as base.</td>
<td>a) Pd/SiO$_2$ (low-acidic) or Cr$_2$O$_3$/$\gamma$-Al$_2$O$_3$ or Pd-Ce/ZSM-5 (acidic); b) Pd/carbon, SiO$_2$ or Al$_2$O$_3$, acidity on the catalyst must be minimal.</td>
<td>[2,10,14,22-27].</td>
</tr>
<tr>
<td>2.</td>
<td><img src="image2.png" alt="Chemical Structures" /></td>
<td>$T = 400^\circ C$, $P_{H_2}$ up to 10 bar, $H_2$/Hydrocarbon $= 10$, WHSV $= 2$, conditions for the Amoco process.</td>
<td>Pt/$\gamma$-Al$_2$O$_3$, catalyst washed with Na$_2$CO$_3$, Na also as promoter.</td>
<td>[1,28-31].</td>
</tr>
<tr>
<td>3.</td>
<td><img src="image3.png" alt="Chemical Structures" /></td>
<td>$T = 210^\circ C$, aliphatic ethers as solvent (polyglycol ether), solvent dilution $&gt; 70%$ w/w.</td>
<td>Pd/carbon, catalyst is added in the reaction mixture with a low molecular weight alcohol.</td>
<td>[32-36].</td>
</tr>
<tr>
<td>4.</td>
<td><img src="image4.png" alt="Chemical Structures" /></td>
<td>a) $T \approx 150-250^\circ C$ at reflux, esters as solvent (trimethylene glycol diacetate); b) $T = 300^\circ C$, $P = 1$ bar, $H_2$ as carrier gas, contact time $= 2-10$ s.</td>
<td>a) Pd/charcoal, no deactivation; b) Pd/$\alpha$-Al$_2$O$_3$, low surface area catalyst, pore sizes 40-400 nm, very selective.</td>
<td>[37,38].</td>
</tr>
<tr>
<td>5.</td>
<td><img src="image5.png" alt="Chemical Structures" /></td>
<td>$T = 200^\circ C$, ramp of $1^\circ$/min, $P = 1-3$ bar, $H_2$ acceptors (dimethyl maleate $\rightarrow$ dimethyl succinate).</td>
<td>Pd/charcoal or Pd/Al$_2$O$_3$, selective at high conversion but very sensitive to impurities.</td>
<td>[11].</td>
</tr>
<tr>
<td>6.</td>
<td><img src="image6.png" alt="Chemical Structures" /></td>
<td>$T = 220^\circ C$, liquid phase with $H_2$ acceptors (diethyl maleate or fumarate).</td>
<td>Pd/charcoal, yield $&gt; 90%$</td>
<td>[12].</td>
</tr>
</tbody>
</table>
### 7. Oxidative dehydrogenation of alcohols to aldehydes or ketones

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) $T \approx 320^\circ C$, 5 bar, WHSV $\approx 0.6$, N$_2$ or H$_2$ as carrier gas; b) $T = 100^\circ C$, liquid phase with solvent and H$_2$ acceptors (S or Se).</td>
<td>Pd/Al$_2$O$_3$ or Pd/SiO$_2$-Al$_2$O$_3$ which was treated with NH$_3$. Yield $&gt; 97%$; b) no catalyst is used.</td>
<td>[9,39].</td>
</tr>
</tbody>
</table>

### 8. Dehydrogenation of alcohols to aldehydes or ketones

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>T $\approx 400^\circ C$, 1 bar, WHSV $\approx 0.4$, N$_2$ as carrier gas, MeOH in excess.</td>
<td>Bi-functional catalyst, base catalyzed alkylation with dehydrogenation, V$_2$O$_5$/TiO$_2$ or Cr$_2$O$_3$/MgO.</td>
<td>[40-42].</td>
</tr>
</tbody>
</table>

### B. Dehydrogenation of alcohols to aldehydes or ketones

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>T $\approx 360^\circ C$, P $\approx 2$ bar, H$_2$ / cyclohexanol $= 3$, LHSV $= 0.4$, H$_2$ and CH$_4$ (1:1 mol/mol) as carrier + H$_2$O.</td>
<td>Bulk ZnO with Al$_2$O$_3$ and sulfates and promoters such as CaO and K$_2$O.</td>
<td>[43].</td>
</tr>
<tr>
<td>T $\approx 265-329^\circ C$, $\uparrow$ 0.25-3$^\circ$C/day, P $\approx 1$ bar, H$_2$:N$_2$:octanol $= 1:9:1$, LHSV $= 0.8$; b) $T = 250^\circ C$, P $\approx 1$ bar, liquid paraffin as solvent, N$_2$ as purging gas.</td>
<td>a) Cu / MgO, C $= 58%$, S $= 99%$, stable catalyst; b) Cu-Cr mixed oxide, C $= 67%$, S $= 91%$.</td>
<td>[44,45].</td>
</tr>
<tr>
<td>a) Oxidative dehydrogenation, T $= 350^\circ C$; b) T $\approx 230^\circ C$, P$_{H_2}$ $\approx 2$ bar, liquid phase reaction without solvent.</td>
<td>a) Group IB metal coated on stainless steel powder (PROPAK ®); b) CuO:Cr$_2$O$_3$ $= 1:1$ or Raney Cu, Yield $= 90%$.</td>
<td>[16,46].</td>
</tr>
<tr>
<td>Gas phase: T $\approx 250^\circ C$, P $\approx 4$ bar, H$_2$/butanediol $= 4$, WHSV $= 3$; Liquid phase: T $= 195^\circ C$ (reflux), P $\approx 1$ bar, catalyst/butanediol $= 5$ w/w.</td>
<td>Cu-Cr catalyst promoted with Mn or Ba, Na or K can also be added. Pure Cu-Cr catalyst has bad abrasion properties in the liquid phase.</td>
<td>[47-50].</td>
</tr>
</tbody>
</table>
1.4. Dehydrogenation to aromatic or heteroaromatic compounds

The use of renewable feedstocks from natural sources is probably a field where heterogeneous catalysis can bring considerable improvements. The dehydrogenation of cheaply available mono-terpenes from the citrus production or the pulp and paper industry to furnish the more commercially valuable p-cymene is a good example (Scheme 1). This reaction has been studied in detail over metallic [2,14,23], oxidic [24,25], and basic [26] catalysts.

Scheme 2 shows two different reaction pathways for converting α-limonene to p-cymene (reaction 1a, Table 1). It was first believed that acid centers are required to isomerize the double bonds into the cyclohexene ring. Once these ring conjugated bonds are formed aromatization can proceed rapidly over the dehydrogenation function of the catalyst. The function can be either based on Cr₂O₃ [24] or Pd [14]. The major problem is the careful control of acid strength to avoid polymerization and isomerization of p-cymene to m-cymene. Krishnasamy and Yeddanapalli have shown that an optimum amount of potassium is favorable over a Cr₂O₃/γ-alumina catalyst [25]. The strong acid sites are neutralized leaving the weak sites unaffected. Weyrich et al. [14,51], on the other hand, used a catalyst based on Pd/ZSM-5 promoted with Ce. They were able to increase the selectivity to p-cymene because of the shape-selective effect of the MFI structure [22].

![Scheme 2: two different reaction pathways for the synthesis of p-cymene from α-limonene](image-url)
The second approach to the conversion of α-limonene to p-cymene is the use of a purely hydrogenation/dehydrogenation catalyst under reducing conditions. For this process Pd supported on a low-acidic silica carrier turned out to be the most appropriate catalyst [23]. Scheme 2 illustrates the possible reaction pathway. In the presence of hydrogen, the isolated double bonds can be hydrogenated very rapidly. An equilibrium is established between p-menthane and p-cymene that is a function of the temperature and the hydrogen pressure (Figure 1). At temperatures of ca 300°C the yield of p-cymene is > 99%. The use of hydrogen makes the conditions milder for dehydrogenation (less coke formation) and no deactivation is observed after more than 100 h on-stream. The reaction is, moreover, slightly exothermic, which is convenient for industrial application. The catalyst has been tested with commercial mixtures of terpenes (dipentene) and the yield remained high (> 95%). The process is now being tested in a scale-up unit and preliminary results have been published [2].

The role of acidity is emphasized when an OH group is present in the α-limonene structure (reaction 1b) [27]. The acidity of the carrier must then be strongly reduced to avoid dehydration. Carriers such as carbon, silica and alumina are appropriate though other forms than γ-alumina are usually used. The introduction of a base such as triethylamine directly into the reaction mixture is also imperative. Considering these restrictions, the temperature of the reaction must not exceed 150°C. Thus, it is essential to reduce the pressure (< 0.01 bar) to increase the yield.

An interesting use of dehydrogenation is the formation of specific alkylpolynuclear aromatic compounds, specifically dimethylnaphthalene (DMN) and dimethylbiphenyl (DMB). They are usually synthesized by alkylation of the corresponding non-alkylated aromatic compound with methanol, and a mixture of compounds is produced which is difficult to separate by distillation. Amoco has developed a four-step commercial process [Scheme 3] based on the side-chain base-catalyzed alkylation of o-xylene with butadiene to form 2,6-DMN [1]. The third step of this process is the dehydrogenation to 1,5-DMN (reaction 2a) [28]. The advantage of first synthesizing 1,5-DMN is that it can be selectively isomerized to 2,6-DMN [29]. The same idea is also applied to form DMB derivatives, i.e. p-xylene is alkylated with cyclohexene or cyclohexanol to form an intermediate that can be further dehydrogenated to 2,5-DMB [30]. A similar method can be used to produce 2,4-DMB from m-xylene [31].
The dehydrogenation to these polynuclear aromatics is quite straightforward. The reaction conditions are similar to catalytic reforming. The reaction is performed in the presence of 10 bar of hydrogen with a hydrogen to reactant ratio of 10. The temperature is relatively high (400°C) and the reaction is fast and selective (> 95%). The catalyst is Pt supported on γ-alumina. The carrier is previously treated with a base (Na₂CO₃) to remove residual chlorine. Excess of Na is maintained on the support to eliminate potential acid centers, which might cause undesired isomerization and cracking of the hydrogenated starting material [28].

\[
\begin{align*}
\text{C}_\text{C} & \quad \text{C} = \text{C} = \text{C} \\
\text{1st step} & \quad \text{Na/K}_2\text{CO}_3 \\
\text{2nd step} & \quad \text{solid-acid} \\
\text{3rd step} & \quad \text{Pd/Al}_2\text{O}_3 \\
\text{4th step} & \quad \text{zeolite} \\
\text{C}_\text{C} & \quad \text{C} \\
\end{align*}
\]

*Scheme 3: Amoco process for the synthesis of 2,6-dimethylnaphthalene.*

The dehydrogenation to aromatic compounds becomes more complex when groups such as hydroxy, carbonyl and acid anhydride are attached to the ring [Table 1, reactions 3-5] [11,32-38]. The reaction is then usually performed under milder conditions in the liquid phase by the use of a solvent. Common solvents are high boiling-point aliphatic ethers or esters and the typical catalyst is Pd on activated charcoal. When the conditions are optimized conversion and selectivity can be very high (> 95%). Reaction 5 is an example of the use of a hydrogen-acceptor molecule (dimethyl maleate). The conditions for reaction 4b deserve a closer look. This reaction is performed in the gas phase with a low surface area catalyst (α-alumina, 5 m²/g). The low surface area probably hinders rapid consecutive reactions of the phenol derivative. These rapid reactions (probably condensation) would inevitably take place in the pores of high surface area supports such as γ-alumina. Thus the use of a low surface-area catalyst has the same effect as adding a solvent to the liquid phase.

The same logic also applies for the dehydrogenation to heteroaromatic compounds. The dehydrogenation is usually simple and straightforward with relatively uncomplicated
molecules such as 3-methylpiperidine (reaction 7a). In this case, β-picoline can be produced in high yield over a classical Pd supported catalyst with conditions similar to the Amoco process [39]. When, however, the reactants become more complex (reaction 7b or 6) hydrogen acceptors, solvents and milder conditions are more practical [9,12]. In the pharmaceutical industry the synthesis of hormones, alkaloids, and vitamins via dehydrogenation is almost exclusively based upon hydrogen acceptors. Chloranil often finds application in the selective dehydrogenation of corticosteroids [13].

An interesting approach to dehydrogenation is a combination with a second reaction, e.g. alkylation. Such so-called ‘one pot reactions’ are performed on bi-functional catalysts. For example, the dehydrogenation of dimethyltetralin can be accomplished with the ring closure reaction to form the cyclohexyl group (Scheme 3). The catalyst, which has dehydrogenation activity due to Pd or Pt, must be combined with acid functionality [29]. The selectivity is increased when both functionalities are physically separated, i.e. an acid catalyst (USY) is well intermixed with a noble metal supported on its own non-acidic support (activated carbon). The noble metal is not directly impregnated on the acidic catalyst. An example of base-catalyzed ‘one pot reactions’ is the alkylation of methanol with cyclohexanol or cyclohexanone to form 2,6-dimethylphenol (reaction 8) [40-42]. For this reaction MgO is impregnated with Cr$_2$O$_3$. MgO has base functionality to alkylate methanol and Cr$_2$O$_3$ is probably the dehydrogenation functionality. Synergy between both metals cannot be excluded. Cr$_2$O$_3$ on MgO can be reduced more easily and the Cr$^{3+}$ ion might show some Lewis acidity character [40,41].

1.5. Dehydrogenation of alcohols to aldehydes or ketones

The synthesis of aldehydes or ketones from the dehydrogenation of alcohols is one chemical route among many possible alternatives. The hydroformylation of olefins is the most utilized synthetic route, although dehydrogenation has found a place in the production of fragrance aldehydes. From the Ullmann Encyclopedia [52], it is apparent that dehydrogenation becomes predominant when the carbon number is C$_8$ or more for straight-chain aldehydes. The unsaturated C$_{10}$ aldehydes from the transformation of essential oils are a second important field where dehydrogenation is often employed (Table 1).
The formation of cyclohexanone from cyclohexanol (reaction 9) is a commercially important reaction and also a good test reaction for many catalysts. The dehydrogenation of cyclohexanol can give three main products, cyclohexanone, cyclohexene and phenol. The product obtained depends on the catalyst functionality and the reaction has often been used to characterize the properties of bimetallic catalysts. A recent example is found in reference [53], where many other references are cited. The commercial catalyst is usually based on ZnO (79%) with promoters such as CaO (6.6%), K₂O (3.3%), Al₂O₃ (4.5%) and sulfates (2.5%, all in wt%) [43]. The reaction is performed at temperatures within the range of 340 to 380°C and under a pressure of 2 bar. For maximum dehydrogenation efficiency it is preferable to use a one-to-one mixture of hydrogen and inert gas (methane) with a hydrogen-to-cyclohexanol ratio of 3. The key element is water, which is introduced in small amounts (1-2 w/w cyclohexanol) to act as a promoter. The optimal LHSV in this case varies between 0.2 and 0.6. The conversion is thermodynamically limited to values up to 80% but the total yield after recycling of the product can be as high as 97%, because of the good reaction selectivity.

The dehydrogenation of long-chain alcohols or unsaturated terpenols is conducted under similar conditions (reactions 10 and 11). It is usually accepted that dehydrogenation is advantageous with primary alcohols to prevent overoxidation to carboxylic acids when oxidation is a competitive method [54]. De Graaf and Delahaye [44] reported that the introduction of water is not always an advantage especially when an azeotrope can be formed. An appropriate gaseous mixture of hydrogen and inert gas can compensate for the lack of water, and hydrogen is introduced only when the reaction has started. When the reactants become more complex the reaction can also be performed in the liquid phase. Addition of a solvent such as liquid paraffin is useful for diluting the system and increasing the thermodynamic yield [45]. Occasionally hydrogenation/dehydrogenation are both applied in the same process as, for example, in the hydrogenation of phenol to cyclohexanol and its consecutive dehydrogenation to cyclohexanone [43]. In a continuous process it is then convenient to use the same flue gas composition to perform the reaction in one pass. In a batch process, it is convenient to find appropriate conditions to perform the process in the same reactor [46].

The presence of functional groups other than alkyl in addition to the OH group makes the dehydrogenation more sensitive to side reactions. The -CH₂OCH₃, -CH₂OC₆H₅, -CH₂N(CH₃)₂, and -CF₃ groups sustain the action of the catalysts at higher temperatures while
the cyano, chloro, bromo, tertiary OH and COOH groups undergo decomposition [55]. A way to partially circumvent the problem is to decrease the temperature and to work under reduced pressure [56]. Substituents also influence the reaction rate. Electron-withdrawing substituents usually reduce the rate [55].

Finally, The dehydrogenation of butanediols to $\gamma$-butyrolactone is an important commercial reaction that was developed by BASF and is one of the so-called Reppe processes. The most probable reaction mechanism via the $\gamma$-hydroxybutyraldehyde intermediate clearly shows that the reaction proceed via two separate alcohol dehydrogenation steps with a rearrangement step taking place in-between (reaction 12) [47]. The reaction is usually performed in the gas phase with hydrogen as carrier gas, to reduce catalyst deactivation, which is a characteristic problem. Thus, extensive research is now being conducted in the liquid phase [48,49]. In addition to a lower catalyst deactivation rate, the liquid phase reaction also reduces the number of side products. The drawbacks are, of course, lower activity but also abrasion problems with the catalyst. The catalyst is preferably stabilized as a powder in a silica matrix (Ludox ®) [49]. The catalyst most often encountered in the patent literature is a Cu-Cr with a promoter such as Ba or Mn. The catalyst is also preferably doped with Na or K and pretreated very carefully in a reducing atmosphere [50].

2. ALKYLATION

Alkylation is of paramount importance in the chemical industry. Large-scale processes such as ethylbenzene, cumene, and alkylated gasoline production are based on acid catalyzed alkylation [1,57]. For the synthesis of more refined molecules with linear structure such as those illustrated in the introduction, the use of zeolites has now become the most popular way [58]. Zeolites have the unique property of shape selectivity that can influence the product distribution of isomers based on their spatial orientation. Alkylation is usually performed with acid catalysts though base and organometallic catalysts have also some applications [59]. Our discussion will however be limited to acid catalyzed alkylation for conciseness.
2.1. Thermodynamic

The reverse of alkylation is cracking and both reactions follow exactly the same mechanism. Cracking is endothermic and performed at high temperatures ($T > 450^\circ$C), so is alkylation exothermic and favored at low temperatures. Figure 2 shows the thermodynamic equilibrium for the cracking of ethylbenzene, cumene and 2-isopropynaphthalene. The transition temperature lies between 300 and 400°C. Ethylbenzene is thermodynamically more stable than cumene and this is one reason why cumene cracks more easily. The second reason is inferred to the formation of a secondary carbocation with propylene which facilitates the alkylation/cracking dangling of cumene, propylene and benzene. Aromatic compounds with a binuclear structure are cracked at even lower temperatures due to the greater stability of the aromatic function. The extension of this principle leads to the formation of coke which is thermodynamically highly favored over the typical alkylation conditions.

![Figure 2: thermodynamic equilibrium conversion for alkylation reactions with an aromatic. Conditions: $P = 1$ bar and initially 1 mol of the alkyaromatic compound (calculation based on the software HSC Chemistry from Outokumpu Research Oy)](image)

The thermodynamic distribution of isomers is of importance to assess the degree of shape selectivity, which is involved in a particular reaction. Table 2 and Table 3 show the equilibrium composition alkylbenzenes, alkynaphthalenes, and alkylbiphenyls. It is observed
a lack of ortho isomers for dialkylbenzenes possessing bulky substituents. The decrease is progressive from xylene to tert-butyltoluene; the later forming no more ortho isomer. Steric hindrances are of course responsible of this behavior. For alkylnaphthalenes, the rate of isomerization and the equilibrium concentration of the 2-isomer are found to increase with increasing branching of the alkyl substituent [60] (Table 3). Finally, for dialkyl binuclear aromatic compounds the selectivity to the most slim isomer (4,4′-diisopropylbiphenyl and 2,6-diisopropynaphthalene) decreases considerably because of the increasing number of other possible isomers.

**Table 2: equilibrium composition of dialkylbenzenes [60,61]**

<table>
<thead>
<tr>
<th>Compound</th>
<th>ortho (%)</th>
<th>meta (%)</th>
<th>para (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylenes</td>
<td>18</td>
<td>58</td>
<td>24</td>
</tr>
<tr>
<td>Ethyltoluenes</td>
<td>7</td>
<td>66</td>
<td>27</td>
</tr>
<tr>
<td>Isopropyltoluenes</td>
<td>1.5</td>
<td>69</td>
<td>29.5</td>
</tr>
<tr>
<td>tert-Butyltoluenes</td>
<td>0</td>
<td>64</td>
<td>36</td>
</tr>
</tbody>
</table>

**Table 3: equilibrium composition of (di-) alkylnaphthalenes or (di-) alkylbiphenyls [60,62,63]**

<table>
<thead>
<tr>
<th>Compound</th>
<th>monoalkylated</th>
<th>dialkylated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-isomer (%)</td>
<td>2-isomer (%)</td>
</tr>
<tr>
<td>(di-) Methylnaphthalenes</td>
<td>24.5</td>
<td>75.5</td>
</tr>
<tr>
<td>(di-) Ethynaphthalenes</td>
<td>9.5</td>
<td>90.5</td>
</tr>
<tr>
<td>(di-) Isopropynaphthalen</td>
<td>1.5</td>
<td>98.5</td>
</tr>
<tr>
<td>(di-) tert-Butynaphthalen</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Compound</td>
<td>3-isomer (%)</td>
<td>4-isomer (%)</td>
</tr>
<tr>
<td>(di-) Isopropylbiphenyls</td>
<td>63</td>
<td>35</td>
</tr>
</tbody>
</table>

The thermodynamic stability of carbocation intermediates is substantially different from the corresponding neutral hydrocarbon. This situation is exemplified when a large excess of superacid such as HF-BF₃ is used for the isomerization of methylbenzenes. In such conditions the most stable arenium ion formed is the 2,4-dimethylbenzenium ion and all other isomers rapidly rearrange into this ion. Thus, it is possible to obtain after alkylation a product composition close to 100% in the meta isomer [60]. The equilibrium composition is then only
function of the carbocation intermediate. The same reason is also involved for the side chain isomerization of isopropylbenzene. n-Propylbenzene is substantially favored although isopropylbenzene is the dominant product after alkylation (vide infra).

### 2.2. Reaction conditions and catalysts

Alkenes, alkynes, dienes, ethers, alkyl halides and alcohols are all potential alkylating agents although large-scale alkylations use almost exclusively alkenes. Alkenes are inexpensive and do not pose the problem of by-products; ethylene and propylene are produced in large amount in a stream cracker. Homogeneous metal halides, the typical Friedel-Crafts catalysts, have been used extensively in the past. Nowadays however, they tend to be replaced by solid acids such as zeolites. Solid acids offer many environmental advantages: (1) they are non-corrosive, (2) they are simple to handle and store, (3) they are easy to regenerate and reuse, and (4) they minimized the formation of by-products [64,65].

Alkylation is always associated with side reactions such as isomerization, transalkylation and coke formation. The experimental conditions must then be carefully tuned to the respective activity of each individual catalyst. Solid acids are usually less active than the typical Friedel-Crafts catalysts and require higher reaction temperatures. A qualitative classification of catalysts acid strength can be drawn as followed [60,66]:

\[
\text{Super acid (i.e. HF-BF}_3^-\text{)} > \text{Friedel-Crafts catalysts (i.e. HCl-AlCl}_3^-\text{)} > \text{HF, H}_2\text{SO}_4^-\text{ > Zeolites > Silica-alumina amorphous oxide > Supported phosphoric acid catalysts (SPA)}
\]

For example, cumene is industrially produced with SPA as well as with AlCl\(_3\) and H\(_2\)SO\(_4\). The later catalysts are quite more active and are used in the liquid phase at temperatures of 40-70°C and at pressures of 5-15 bar. On the other hand, SPA is used in the gas phase at temperatures of 175-225°C and at pressures of 30-40 bar. Although SPA is less active it accounts for 80-90% of the world’s cumene production. Zeolites are now being developed to replace SPA by companies such as DOW-Kellogg, CDTech-Lummus, UOP and Enichem [67,68].
Ethylene is quite more difficult to activate than propylene due to the formation of a primary carbocation. Hence, SPA becomes a too weak catalyst and the currently industrial process employs an AlCl\(_3\) catalyst. Small amount of HCl is added to the feed in order to activate the catalyst. Under these conditions the reaction temperature is around 100°C with the pressure slightly above atmospheric. A more recent development by Mobil-Badger uses zeolite ZSM-5 [57]. It is operated at quite higher temperatures and pressures (400-450°C, 15-30 bar) and gives consequently a broader spectrum of alkylated products. This problem is nevertheless minimized by the unique transalkylation property of zeolites, which ensure high yield of ethylbenzene. Transalkylation is barely observed over Friedel-Crafts catalysts.

2.3. Mechanism

Acid catalyzed reactions are based on carbocation chemistry. The order of stability of carbocation follows this trend: tertiary > secondary > primary. Scheme 4 to Scheme 7 show the typical chemistry encountered for alkylation (Scheme 4), for side-chain isomerization (Scheme 5), positional isomerization (Scheme 6), and transalkylation (Scheme 7) [60]. These mechanisms have all in common the fact that they try to minimize as much as possible the formation of primary carbocations. Tertiary carbocation have relatively long lifetime stability and will consequently take part more easily in intermolecular reactions such as hydrogen transfer and alkylation. In the subsequent drawing the negative counter ion has been omitted but it must always been kept in mind that this ion always exists in close proximity and that a considerable degree of covalent bonding between the carbocation and the anion might prevail [69].

Alkenes are almost exclusively activated with Brönsted acid sites. Lewis acids have little or no activity when used in a pure state [60]. Lewis acids are activated by the presence of impurities or by addition of small amount of co-catalysts as promoters such as water, HCl or alcohols. Thus, protic acids must always be used for alkylation with alkenes. Hydrated solid acids usually fulfill this requirement.

The alkylation of toluene with propylene, as depicted in Scheme 4, will primarily form an isopropyl group attached to the aromatic due to the higher stability of the secondary carbocation. The p-isomer will be kinetically preferred owing to the p-orientation of the
methyl group present on toluene. This methyl group will also increase the nucleophilicity of
the aromatic and will consequently increase its reactivity. Indeed, the product of alkylation are
generally more reactive than the reactant and consecutive serial reactions can easily take
place. The mechanism depicted in Scheme 4 can be viewed as an Eley-Rideal mechanism.

Scheme 4: alkylation mechanism with toluene and propylene

Once p-cymene (p-isopropyltoluene) has been formed it can further react to n-propyltoluene
via side-chain isomerization (Scheme 5) or to m-cymene via positional isomerization (Scheme 6). The formation of o-cymene is more or less forbidden (see section 2.1). It is
surprising to note that n-propyltoluene is thermodynamically favored over p-cymene. The
reaction mechanism is explained by invoking the formation of the most stable benzylic
carbocation that then undergoes rearrangement via an intermediate phenonium ion (Scheme 5)
[60]. Hence once n-propyltoluene has been formed it will not easily isomerized back to p-cymene due to the involvement of a primary cation. On the other hand, the intermediates involved for positional isomerization are identical with those of the alkylation. Consequently the methyl or propyl group migration in p-cymene will arise from a simple 1,2 alkyl shift.

Scheme 6: positional isomerization mechanism with toluene

Transalkylation occurs through a 1,1-diarylalkane intermediate [Scheme 7]. Hence the carbon located in the \( \alpha \) position on the alkyl group will determine the transalkylation rate. It is than obvious that low reactivity is observed for toluene due to the involvement of a primary benzyl
cation. Thus, the reactivity of akyl groups to take part in transalkylation increases in the order methyl < ethyl, propyl < isopropyl.

Coke formation is the less well-understood mechanism [69]. It is always present with acid catalyzed reactions and causes deactivation. Coke usually consists of polyaromatic condensed-ring structure, which approaches the character of graphite. In some cases, however, it is attributed to a rapid polymerization of alkenes. The hydrogen to carbon ratio is then substantially higher and the term carbonaceous deposit should be used instead of coke. The foregoing statements summarize the important characteristics of coke formation during acid catalyzed reactions:

1. The rate of coke formation intensifies with increasing acid strength, with increasing temperature, and with increasing base strength of the reactants.

2. The acid site density plays an important role on coke formation. High density, i.e. with many acid sites in close proximity, favors hydrogen transfer reactions and as a result coke formation is facilitated. Zeolite dealumination procedures are good methods to reduce the acid density and consequently the rate of coke formation.

3. Coke formation is further intensified when a hydrogen acceptor is present with a coke precursor. Hydrogen acceptors are for example α-olefins like propylene and coke precursors are usually aromatic compounds like benzene. This situation is always encountered when an aromatic system is alkylated with an olefin. In such a case, benzene can rapidly be transformed into a polyaromatic compound because olefins can easily catch the hydrogen evolved from the graphitization process reducing the thermodynamic constraint.

2.4. Shape selectivity

Zeolites have the remarkable property of shape selectivity [70]. They are crystalline silica-alumina that possesses micropores. The micropores are in the dimension of typical molecules and if the active centers are located in these micropores the reaction is strongly influence from steric factors. For example, the 8-membered ring zeolite erionite can discriminate between
n- and iso-paraffins and was used by Mobil in the Selectoforming process [8], which selectively hydrocracked n-paraffins in reformate to improve the octane number of the liquid product. On the other hand, the 10-membered zeolite ZSM-5 is usually the most appropriate catalyst for reaction involving the benzene ring such as alkylation of toluene to para products (p-xylene, p-cymene) [57]. Finally, the 12-membered ring zeolite mordenite is useful for multinuclear aromatic compounds such as those depicted in Scheme 10. Propylene is, however, required to obtain shape selective effects which shows that the dimension of the desired molecule must be in close relation with the pore apparatus of the zeolite.

Figure 3: different types of shape selectivity
Figure 3 shows the three types of shape selectivity that are usually encountered [71,72]. The selectivity depends whether on a limitation of the entrance of reactant, on a limitation of the departure of products, or on the formation of certain transition states:

1. Reactant selectivity occurs when the size of some molecules in a feed is small enough to diffuse though the pores of a zeolite.

2. Product selectivity occurs when the size of some product molecules is too bulky to diffuse out of a zeolite. They can further react and be converted to the desired product or be transformed to coke.

3. Restricted transition-state selectivity arises when insufficient space is available in the pores for two molecules to come together.

It follows that reactant and product selectivities are function of diffusion. The zeolite crystal size as well as the temperature will have important influences. The activation energy for diffusion is lower than for the activation energy for the reaction, therefore at higher temperatures the reaction will be mostly diffusion limited. The result is that at higher temperatures the selectivity will increase instead of decreasing as it is usually the case.

2.5. Alkylation of biphenyl and naphthalene with propylene

There are some advantages to use 4,4′-diisopropylbiphenyl (4,4′-DIPB) and 2,6-diisopropyl-naphthalene (2,6-DIPN) as intermediates for the production of the corresponding dicarboxylic acids as shown in Scheme 10. Firstly, they are more easily oxidized than their methylated counterparts 4,4′-dimethylbiphenyl (4,4′-DMB) and 2,6-dimethylnaphthalene (2,6-DMN). Secondly, shape-selective alkylation is more facile with propylene than with methanol over 12-membered ring zeolites such as mordenite. The shape-selective methylation of biphenyl and naphthalene with methanol has been reported over a 10-membered ring zeolite (ZSM-5) though the conversion is severely limited from diffusional resistance [73,74]. The shape selectivity has been attributed to the external surface sites of zeolite ZSM-5 which perfectly suit small-size naphthalenic compounds [73]. Matsumoto et al. [75] studied the alkylation of biphenyl with different size reactants over a 12-membered ring zeolite and found out that the
reaction becomes shape-selective from propylene or larger molecules. Ethylation had a very low selectivity to the desired linear isomer.

The most appropriate zeolite for the isopropylation of biphenyl [76,77] and naphthalene [63,78] is a dealuminated mordenite. Other interesting candidates are SAPO-11 and ZSM-12 zeolites [62,79,80]. On the other hand, silica-alumina, zeolites Y and L are considered non-shape-selective [78,81]. Zeolite beta has an ambivalent position. It has been reported as a shape-selective catalyst [82] but also as a non-shape-selective catalyst [83]. The zeolite activity decreases in the order: silica-alumina > Y > beta > mordenite [78,84]. Silica-alumina has usually a lower density of acid sites and is expected to have the lower activity unless the reactions in zeolites are highly diffusion limited [85]. This situation is even amplify with zeolite mordenite, which possesses a one-dimensional pore structure and has consequently the lower activity.

Zeolite mordenite has an intrinsic good selectivity for the alkylation reaction but a dealuminated mordenite is even better in terms of activity and selectivity. Many reasons have been suggested in the literature for this behavior and still there is debate concerning the actual role of dealumination. The opinions of different research groups are summarized as follows:

1. The group belonging to DOW Chemical suggested that dealumination creates new mesopores in zeolite mordenite which facilitates diffusion of reactants [86]. This view, which is also shared by Song and Schmitz, [87] is based on a large experience of dealumination of zeolite mordenite. The DOW cumene process is now based on such a zeolite called 3-DDM for three dimensional dealuminated mordenite [68]. The increase of shape-selectivity is explained by an increase of the constrain index obtained from XRD [76]. In other words, the pores of zeolite mordenite become slightly smaller as a consequence of the increasing SiO$_2$/Al$_2$O$_3$ ratio.

2. The group of Sugi from Tsukuba in Japan proposed that coke formation is the main factor influencing the activity and selectivity. Coke rapidly blocks the pore entrance as a consequence that only the non-selective sites at the external surface are active for the alkylation [88,89]. Dealumination remarkably reduces the coke formation permitting the reaction to proceed within the pores so that the intrinsic shape-selective properties of zeolite mordenite are expressed. Dealumination decreases the number of acid sites, which
reduces coke formation permitting an increase of diffusivity of reactants and products. Moreover, this group explicitly stated that neither a preferential dealumination of the external surface area nor a creation of new mesopores is responsible for the increase in activity and selectivity [89].

3. Matsuda et al. claimed that the acid strength is the main factor influencing the activity. Strong acid sites favor side reactions such as oligomerization of propylene, isomerization of products, and rapid coke formation. They showed that even a zeolite mordenite with a higher SiO$_2$/Al$_2$O$_3$ ratio could rapidly loose selectivity of linear products due to isomerization at high conversion [90]. The partial neutralization of acid sites with sodium increases the 4,4’-DIPB yield due to the suppression of isomerization [83].

From our point of view, the second point is the most probable explanation of the dealumination effect. The increase of the constrain index is a well-known behavior for zeolite X where a large amount of aluminum is present (SiO$_2$/Al$_2$O$_3$ = 2.5) [69]. The removal of framework aluminum leads to a small contraction of the zeolite structure. However, this behavior would be marginal for the dealumination of zeolites with larger SiO$_2$/Al$_2$O$_3$ ratio. The third point assumes that alkylation proceeds on weaker acid than isomerization. However, from Scheme 4 (alkylation mechanism) and Scheme 6 (positional isomerization mechanism) the same arenium ion is observed which causes both reactions to be equally feasible.

The methods of dealumination can be of various types. Acid leaching is a common method used to dealuminate zeolite mordenite. In contrast, Fellmann and his team recommended a steaming procedure before the acid treatment to obtain stable catalytic activity [63]. The 3-DDM synthesis is apparently based on a high temperature calcination followed by a concentrated nitric acid treatment. Vergani et al. investigated the benefit for this combined approach and found out an improved dealumination [91]. The passivation of the external surface area is also a way that should not be neglected for catalyst optimization. Chemical vapor silanation [92], cerium impregnation [93], and tributylphosphite poisoning [90] are all methods that increase the selectivity to the slim isomer. Nevertheless, the rate of coke formation remains high.

The dealumination of zeolite mordenite is generally accompanied by a decrease in the number of acid sites and by an increase in diffusivity. The interaction of both phenomena leads to an
optimal SiO$_2$/Al$_2$O$_3$ ratio for maximal activity. This ratio has been determined to be very large for references [77,86], between 140 and 160 for reference [91], and around 40 for reference [63]. This variation shows that a complex interaction of factors accounts for the activity. In contrast, the selectivity increases rapidly with the increase of the SiO$_2$/Al$_2$O$_3$ ratio, level off at a value of 25 and slightly increases afterwards [81]. The selectivity of 4,4’-DIPB in DIPB is as high as 85% while the selectivity of 2,6-DIPN in DIPN is around 65%.

The different catalytic aspects stated so far are relevant for both alkylations (biphenyl and naphthalene). There are nonetheless important differences which must be clarify. The alkylation of biphenyl with propylene is a typical restricted transition-state selectivity [94]. This is, however, not the case for the alkylation of naphthalene where both 2,6- and the 2,7-DIPN can be formed. The discrimination between these isomers is then attributed to the better diffusion of the 2,6 isomer which describes a product selectivity [95]. The reaction is to some extent also a reactant selectivity because the bulky mono-isopropylated compounds (2-IPB, 3-IPB and 1-IPN) cannot enter the micropores of zeolite mordenite to further react.

There are also major differences in the interpretation of results for both reactions. As shown in Table 3 the formation of the beta-isomers (2-IPN, 2,6-DIPN and 2,7-DIPN) is thermodynamically preferred although the kinetic alkylation gives mainly the 1-isomers. The situation is exactly the opposite for the alkylation of biphenyl. Thus, great care is needed in the interpretation of catalytic results; the selectivity values should always be given as a function of conversion. The concentration ratio of both slim isomers (2,6-DIPN/2,7-DIPN) is also a good indication of shape selectivity. For silica-alumina the value is close to 1 while for a dealuminated zeolite mordenite the value approaches 3. Other selectivity values such as propylene oligomers and solvent cracking products should also be considered [85]. These variables are very much influenced by the reaction conditions and the type of reactor used.

Commercial processes for the production of cumene use benzene to propylene ratios from 5 to 7 in order to minimize side reactions associated with propylene [67]. The majority of studies for the alkylation of biphenyl and naphthalene has been performed batch wise in slurry reactors by maintaining a constant pressure of propylene over the reacting liquid. The propylene concentration is then limited from its solubility in the liquid phase. Figure 4 shows the propylene solubility as a function of temperature at a total pressure of 10 bar (autogenous propylene pressure at 22°C). As it is expected, the solubility increases with a decrease in
temperature. At 200 and 250°C, the solubility remains between 5 and 7 mol% which is in a safe range to avoid side reactions. The presence of propylene also reduces the rate of isomerization of products which is another advantage to maintain a constant pressure of propylene [96]. For example, 4,4’-DIPB will not be easily isomerized to the more stable 3,4’-DIPB. This aspect probably explains the difference in results obtained by different research groups operating a slurry reactor or operating a fixed bed reactor. In the case of a fixed bed, the decrease in propylene concentration along the packed bed might conduct to an increase of isomerization in the bottom of the reactor. The occurrence of 1-substituted alkyl-naphthalenes becomes very low and worn interpretation can lead to over-evaluation of shape-selective effect. In practice, the 2,6/2,7 ratio is quite more convenient.

![Figure 4: solubility of propylene in biphenyl and naphthalene as a function of temperature](thermodynamic calculations based on a Grayson-Streed modified Chao-Seader model evaluated on ChemCAD from Chemstations Inc.)

The temperature has a similar effect as the propylene pressure [97]. At high temperatures the propylene solubility is reduced which favors isomerization. High temperatures promote also a rapid coke formation that readily deactivates the acid sites located in the micropores as a consequence that only the external surface area remains active. In contrast, the temperature can have a positive effect on the selectivity when the reaction is reactant and product limited. The selectivity to the most slim isomer should than increase with an increase of the temperature until the appearance of side reactions.
The use of different alkylating agents other than propylene influences also the selectivity. Isopropylbromide produces the same amount of 2,6- and 2,7-DIPN [92]. On the other hand, the use of isopropanol increases the selectivity although the activity decreases [98]. The beneficial role of isopropanol is explained by the generation of water in-situ during the reaction. The water reduces coke formation and passivates the external surface area to some extent [99]. It is worthwhile to note, that over a dealuminated zeolite mordenite the addition of water has even a promoting effect. As a matter of fact, it is able to transform the framework Lewis acid sites to Brönsted sites turning them into active catalytic centers.

3. ULLMANN COUPLING

3.1. Classical Ullmann coupling

The Ullmann reaction is a classical organic synthesis method for the coupling of aromatic molecules which uses Cu-powder as stoichiometric reagent [100]. For example, iodobenzene is coupled to biphenyl and in a similar way p-iodotoluene is used to form the linear molecule 4,4’-dimethylbiphenyl (4,4’-DMB) [101]. The classical Ullmann reaction is usually limited to the use of iodo and to some extend bromo compounds [101,102]. It is also more efficient with molecules having electron deficient aromatic ring such as in iodo-nitrobenzene. Nevertheless, the yield remains modest even for o-iodo or o-bromo-nitrobenzene in where the ortho position is advantageous (around 65%) [102]. It should be noted that m- and p-chloro-nitrobenzene are totally ineffective for the reaction. Hence, the production of cheap intermediate chemical from chloro compounds is impracticable by the Ullmann reaction. Nevertheless, the Ullmann reaction remains useful in the pharmaceutical where alkaloids can be synthesized via this method and where haloanthraquinones can be coupled to form important intermediates for the production of pyranthrone and flavanthrone [103].
3.2. Modified Ullmann coupling

For the last 25 years there has been a great deal of research performed to improve or adapt the Ullmann reaction to other conditions and reactants. Several metals including Ni [104], Pd [105] and Pt [106] have been shown to enter into oxidative addition from a zero valent state with aromatic halides to give the subsequent aryl-aryl formation. In the case of Ni, Semmelhack et al. [104] showed that a zero valent Ni could readily take over the function of Cu as stoichiometric reagent. Ni is used in a ligand environment with 1,5-cyclooctadiene (Ni(COD)₂) which increases the reactivity of the metal. As a consequence, the reaction temperature is quite lower than the reaction temperature of the classical Ullmann reaction. However, the system is very sensitive to protons and dehalogenation can easily occur when functional groups are present such as hydroxyl or carbonyl [107]. Consequently, an aprotic polar solvent like dimethylformamide is also required. Following the above mentioned work, Vandesse et al. [108] suggested the use of sodium hydride as a reducing agent in a complex mixture of sodium hydride, alkoxyde and organometallic Ni with ligands such as Ph₃P or 2,2'-bipyridine. Also, Colon and Kelsey [109] introduced the concept of a sacrificial metal as electron donor for the regeneration of Ni where metals like Zn, Mg, and Mn are used. The major improvement of those methods is the capability to couple aryl chloride molecules. Similar to those methods is an electrochemical alternative [110].

3.3. Catalytic alternative

An interesting heterogeneous catalytic alternative of the aforementioned reaction with zero valent metal is the result obtained by Bamfield and Quan [111]. The synthesis of biaryls is achieved by the use of a Pd catalyst supported on charcoal. The reaction mixture consists of two liquid phases where the organic phase is the aryl halide and where the aqueous phase is a high concentration of NaOH and sodium formate in water. The introduction of a surfactant is also essential for the reaction. In this mixture, sodium formate plays the role of hydrogen donor to react with chlorine on the catalyst surface while NaOH neutralized HCl that formed consequently. It is very fortunate to see a yield up to 55% to 4,4’-dimethylbiphenyl (4,4’-DMB) using p-chlorotoluene (PCT) in the presence of a hydrogen donor molecule. Therefore,
the main parallel side reaction is dechlorination. The selectivity of this reaction can be increased as disclosed in a patent referred to the Hoechst AG company [112]. The main improvement is the utilization of polyethers or mixture of polyethers to take over the role of the surfactant employed by Bamfield and Quan. The molecule 4,4’-difluorobiphenyl can be synthesized in good yield from p-chloro-fluorobenzene. Nevertheless, the use of a high amount of base, expensive reducing agents and highly complex reaction mixtures are still important drawbacks for industrial applications.
C. RESULTS AND DISCUSSION

1. DEHYDROGENATION OF PINENES TO p-CYMENE

The main use of p-cymene is its transformation to p-cresol. At the moment, p-cresol is mainly produced via the alkylation of toluene with propylene, followed by oxidation and hydroperoxide cleavage [113]. The alkylation and isomerization steps produce a mixture of cymenes rich in m- and p-isomers. The isomer separation in order to obtain pure p-cresol can be performed with either the cymene or the cresol mixture. For example, UOP developed the Cymex process where m- and p-cymene are separated chromatographically using an appropriate sorbent (molecular sieve) and a desorption medium (toluene) [114]. On the other hand, the cresol isomers can be isolated by partial crystallization of m-cresol under elevated pressure [115], though the strategy adopted now from Sumitomo is based on the subsequent isobutylation of m- and p-cresols followed by distillation and back-dealkylation to m-cresol. Using this route, the widely used antioxidant 2,6-di-tert-butyl-p-cresol is produced directly from p-cresol [113]. Direct syntheses to p-cymene have also been investigated using a ZSM-5 catalyst to obtain a shape-selective effect during the toluene alkylation [57].

A more refined route to p-cymene could start from the transformation of terpenes having a similar structure. Terpenes are naturally occurring renewable materials that can be used as feedstock. It has already been shown that α-limonene [2,10,14,51], 3-carene [24], α-pinene [116] and mixtures of terpenes [23,117] convert to p-cymene in good yields, producing elementary hydrogen. A commercial use of these materials will, however, be limited from their low price availability, which must be compared to the market price of toluene and propylene. α-Limone for example is a by-product from the citrus industry but has recently become a high demand biodegradable solvent, making it an impractical synthetic raw material [118].

Crude sulfate turpentine (CST) has now become the cheapest and the major source of terpenes in Europe and North America [118]. It is a by-product from the pulp and paper industry produced during the pulp digestion in a Kraft paper mill. The market price of CST is variable but low (0.15-0.21 $/kg) and cheaper then starting materials such as toluene (0.26 $/kg) and...
propylene (0.44 $/kg) [118,119]. Unfortunately, it is always contaminated with high concentrations of sulfur which must be reduced prior to its utilization. The exact CST composition is a function of the geographical origin of the wood: for Eastern Canada and Southeastern USA the major component is \(\alpha\)-pinene, whereas for other origins 3-carene may be the dominant compound.

The goal of this work is to convert CST to p-cymene in high yields over Pd based catalysts. The CST used in this work originates from a Kraft paper mill located in La Tuque (Canada) and is composed for over 90% out of \(\alpha\)- and \(\beta\)-pinenes. Thus, the catalytic reactivity associated with a bicyclic terpene such as \(\alpha\)-pinene is investigated in detail, as well as the direct use of CST.

1.1. \(\alpha\)-Pinene versus \(\alpha\)-limonene over silica based catalysts

Previous work of our group on this subject mainly concerned the transformation of \(\alpha\)-limonene to p-cymene for which Pd supported on a weak acidic silica carrier turned out to be the most effective catalyst [2]. It was shown that the acidity has no real influence on the reaction pathway and that a purely hydrogenation/dehydrogenation mechanism takes place. Indeed, the isolated double bonds of \(\alpha\)-limonene can be hydrogenated rapidly in the presence of hydrogen. Equilibrium is afterwards established between p-menthane and p-cymene that is a function of temperature and hydrogen pressure. At temperatures of 300°C, the yield of p-cymene is nearly 99%. The same catalysts were also tested with commercial terpene mixtures obtaining yields as high as 95% but dependent on the terpene composition [23].

The optimal reaction conditions for the conversion of \(\alpha\)-limonene were found to be similar to those used in catalytic reforming although milder in terms of pressure and temperature. As in the case of catalytic reforming, the use of hydrogen in the feed is essential to avoid rapid catalyst deactivation (vide infra). Hence, the reactions are performed under a hydrogen/terpene molar ratio of 4. The atmospheric pressure allows for a reduction in temperatures down to 300°C with still a complete transformation into aromatic compounds. The weight hourly space velocity (WHSV) was set at about 3 h\(^{-1}\), which brings the reaction to
completion in one single pass. Contrary to catalytic reforming, the reaction is slightly exothermic and the heat transfer hindrance is minimized [2].

The first objective of this work is to investigate the transformation of $\alpha$-pinene with the silica based catalysts under the optimal reaction conditions found for the conversion of $\alpha$-limonene (Figure 5). Clearly, the catalytic conversion of $\alpha$-pinene to p-cymene is not as straightforward as for $\alpha$-limonene. The yield is highly variable and appears to be a function of the carrier used, whereas for $\alpha$-limonene the yield is high for all catalysts.

Two main factors are expected to control the catalytic selectivity, namely the metallic dispersion and the support acidity. Figure 6 shows the CO chemisorption isotherms and Figure 7 the ammonia TPD profiles for the three silica based catalysts whereas Table 4 summarizes all these results. For the conversion of $\alpha$-limonene, it has already been demonstrated that the acidity has little influence on the yield of p-cymene [2]. The small difference in conversion observed for these catalysts appears to correlate with the metal dispersion. The dispersion and the yield decrease in the order Pd/D-11-10 > Pd/Aerosil > Pd/Silicalite. For first and second order reactions performed in integral fixed bed reactors,
most of the reactor volume is devoted for the increase of the conversion in the upper fraction, for example from 80 to 99%. Consequently, the variation in conversion between two catalysts of different dispersion will be small even if the difference in dispersion is high.

Figure 6: CO chemisorption isotherms of the silica based catalysts

Figure 7: ammonia TPD profiles of the silica based catalysts
The situation is less clear for the transformation of α-pinene in which the acidity might play an important role. Pd/Aerosil is almost free of acid sites and the yield of p-cymene is less than 10%. Pd/Silicalite has the most and also the strongest acid sites though an intermediate yield of p-cymene. The chemisorption data indicate that the Pd particles are too large to fit in the micropores of silicalite. Thus, the active metal is not in intimate contact with the acid sites and Pd/Silicalite becomes a poor reference catalyst. Moreover, Pd/Silicalite shows also deactivation for the conversion α-limonene as well as for the conversion of α-pinene. It is difficult to synthesize a silicalite free of impurities and consequently these impurities can form strong acid sites that deactivate readily. On the other hand, Pd/D-11-10 is the most selective catalyst with probably the most appropriate acid sites.

Table 4: important characteristics of the silica based catalysts

<table>
<thead>
<tr>
<th>Silica based catalysts:</th>
<th>Pd amount (%)</th>
<th>BET surface area (m²/g)</th>
<th>Acidity (n(NH₃)/g)</th>
<th>Dispersion (%)</th>
<th>Pd crystallite diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/D-11-10</td>
<td>0.52</td>
<td>170</td>
<td>120×10⁻²</td>
<td>58</td>
<td>1.9</td>
</tr>
<tr>
<td>Pd/Aerosil</td>
<td>0.50</td>
<td>190</td>
<td>15×10⁻²</td>
<td>30</td>
<td>3.7</td>
</tr>
<tr>
<td>Pd/Silicalite</td>
<td>0.50</td>
<td>360</td>
<td>190×10⁻²</td>
<td>20</td>
<td>5.6</td>
</tr>
</tbody>
</table>

1.2. Role of acidity

The isomerization of α-pinene over solid acids is a well-known reaction leading to bicyclic products of the camphene series and to monocyclic products of p-menthadienic structure [120-123]. Camphene is industrially produced from the isomerization of α-pinene over a weakly acidic hydrated TiO₂ catalyst [124]. It is suggested in the literature that strong acid sites and high temperatures favor p-menthadienic compounds and that weak acid sites and low temperatures favor camphenic compounds [121,122]. The catalyst acidity plays for sure a key role in the dehydrogenation of a bicyclic compound such as α-pinene to p-cymene contrary to the dehydrogenation of a monocyclic compound such as α-limonene where the acidity has no influence.
To investigate the role of acidity, six catalysts with varying acidity are prepared. The catalysts are presented in Table 5 with their respective Pd concentration, BET surface area, metal dispersion and acidity measurement. The Pd content on all catalysts has a high dispersion, which accounts for a good comparison of their metallic activity (one exception is Pd/H-ZSM-5). The catalysts can be divided in three groups. The first group of catalysts (Pd/H-ZSM-5 and Pd/H-MOR) are zeolitic materials with strong acidity. The second group (Pd/D-11-10 and Pd/D-11-10) are typical supported catalysts with moderate acidity and the last group (Pd/Carbon and Pd-Na/D-11-10) have very weak acidity. Although the general trend in the acidity of each group is obvious, test reactions are used to compare the individual catalysts. The isopropanol dehydration results show that D-10-10 (γ-alumina) is a very active material. It dehydrates isopropanol in almost 100% yield to propene and water. On the other hand, D-11-10 is less active and dehydrates isopropanol in only 30% yield. The last two catalysts have only low residual activity and it is very difficult to differentiate between them. The catalytic activities for the alkylation of biphenyl with propylene confirm the same trend: H-MOR > D-10-10 > D-11-10.

Table 5: important characteristics of the catalysts with varying acidity

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Notes</th>
<th>Pd (%)</th>
<th>BET surface area (m²/g)</th>
<th>Dispersion (%)</th>
<th>Alkylation* / Dehydration activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/H-ZSM-5</td>
<td>MFI structure</td>
<td>0.47</td>
<td>350</td>
<td>10</td>
<td>---**</td>
</tr>
<tr>
<td>Pd/H-MOR</td>
<td>Dealuminated</td>
<td>0.54</td>
<td>550</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>Pd/D-11-10</td>
<td>γ-Alumina</td>
<td>0.55</td>
<td>190</td>
<td>&gt;80</td>
<td>14</td>
</tr>
<tr>
<td>Pd/D-11-10</td>
<td>Silica</td>
<td>0.52</td>
<td>180</td>
<td>58</td>
<td>0.1</td>
</tr>
<tr>
<td>Pd/Carbon</td>
<td>Activated carbon</td>
<td>0.80</td>
<td>1100</td>
<td>65</td>
<td>---</td>
</tr>
<tr>
<td>Pd-Na/D-11-10</td>
<td>Silica with 1% Na</td>
<td>0.51</td>
<td>175</td>
<td>61</td>
<td>---</td>
</tr>
</tbody>
</table>

* Alkylation conditions: T=250°C, P = 10 bar of propylene, Duration = 3 h, biphenyl = 20 g and catalyst weight = 0.5 g
** Biphenyl is too big to enter the pores of a MFI structure

The choice of these catalysts is of course justify from their different acid strength but also for the following reasons. Pd/D-11-10, based on silica, is the most optimal catalyst for the dehydrogenation of α-limonene. On the other hand, Pd/D-10-10, based on γ-alumina, is a common material used to obtain bifunctional catalytic properties with a metal [69]. Pd-Na/D-11-10 is the same material as Pd/D-11-10 with the exception that 1% sodium has been added by impregnation to neutralize the acid sites. Carbon is usually seen as a neutral support that can achieve high metal dispersion [125]. On the opposite, the two zeolitic
catalysts have in addition to strong acid sites the potential to reveal shape-selective properties. H-MOR is a dealuminated material prepared by acid leaching with a SiO$_2$/Al$_2$O$_3$ ratio of 130. Such a zeolite was shown to minimize side reactions in the isomerization of α-pinene to camphenic and p-mentadienic compounds [123]. Alternatively, H-ZSM-5 with a SiO$_2$/Al$_2$O$_3$ ratio of 75 has a MFI structure that has demonstrated shape-selective properties for the formation of p-cymene [22]. Moreover, Pd/H-ZSM-5 is considered to have more acid sites than Pd/H-MOR due to its lower module.

The results for the transformation of α-pinene over the aforementioned catalysts are presented in Figure 8. Clearly, an optimal acid strength is required to obtain p-cymene in high yields. The highest p-cymene yields are obtained over Pd/D-10-10 and Pd/D-11-10 which show almost identical yields of ca. 65%. With an increasing acidity, the formation of products other than C$_{10}$ (lights and heavies) is favored which is the case of catalysts Pd/H-ZSM-5 and Pd/H-MOR. They also show a very fast deactivation caused by a rapid coke formation in the first minutes of time on stream (TOS). On the opposite, more hydrogenated bicyclic and monocyclic products are formed upon a decreasing acidity. The results suggest that strong acid sites are responsible for oligomerization and cracking, that moderate acid sites are responsible of C$_{10}$ isomerization, and that the absence of acid sites favor hydrogenation and
saturation of bicyclic terpenes. However, the real situation is more complex and additional results are required to understand the complex reaction mechanism.

1.3. Acid cracking versus hydrogenolysis

The complexity of the reaction pathway arises from the cyclobutane ring present in α-pinene which has to be selectively opened to a p-menthadienic structure followed by a further dehydrogenation to p-cymene. Scheme 8 shows the four different products that can be formed from different C-C ruptures of the cyclobutane ring.

Scheme 8: four different types of compounds observed from various C-C cleavage of the cyclobutane ring of α-pinene

Here, three types of mechanisms can selectively break the four membered ring, namely acid cracking, C-C hydrogenolysis and thermal fission. As already mentioned, acid cracking will be selective in the C-C bond cleavage between carbon 1 and 6, producing p-cymene after dehydrogenation; the driving force being the intermediate tertiary carbenium ion. Similarly, the same type of products are also expected from thermal fission owing to the greater stability of the tertiary free radical [126]. The cleavage of the bond between carbon 5 and 6, which would lead to o-cymene upon dehydrogenation, is negligible due to steric hindrance [61]. On the other hand, C-C hydrogenolysis can in theory form all four types of products. Ipatieff et al. [127] have, however, demonstrated that under destructive hydrogenation of pinane the cleavage of the bonds between carbons 1 and 7 and carbons 5 and 7 is preferred producing...
predominantly 1,1,2,3- and 1,1,2,5-tetramethylcyclohexanes. As a matter of fact, the appearance of these compounds is a good indication of the catalyst hydrogenolysis activity in the presence of hydrogen [128].

Table 6: the product distribution as a function of different reactants and catalysts ($T = 300^\circ C$, $P = 1$ bar, WHSV = 6 h$^{-1}$, reactant/H$_2$ molar ratio = 4, catalyst weight = 1 g)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reactants</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Selectivity (%)</th>
<th>Selectivity (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aromatics</td>
<td>Bicyclics</td>
<td>Monocyclics</td>
<td>Unsaturated</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>α-Pinene</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>D-11-10</td>
<td>α-Pinene</td>
<td>100</td>
<td>3</td>
<td>0</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Pd/D-11-10</td>
<td>α-Pinene</td>
<td>100</td>
<td>67</td>
<td>6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pd/D-10-10</td>
<td>α-Pinene</td>
<td>100</td>
<td>68</td>
<td>4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pd/Carbon</td>
<td>α-Pinene</td>
<td>100</td>
<td>40</td>
<td>28</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pd/D-11-10</td>
<td>Pinane</td>
<td>87</td>
<td>60</td>
<td>8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pd/Carbon</td>
<td>Pinane</td>
<td>21</td>
<td>33</td>
<td>44</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pd/D-11-10</td>
<td>Camphene</td>
<td>100</td>
<td>18</td>
<td>74</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Pd/Carbon</td>
<td>Camphene</td>
<td>100</td>
<td>1</td>
<td>98</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

To be able to differentiate between the reaction pathways (hydrogenation/dehydrogenation, isomerization, hydrogenolysis and thermal fission), the suspected intermediates pinane and camphene as well as α-pinene are used as substrate. The catalyst supports (silica or carbon) are either weakly acidic or non-acidic and the reaction conditions are the same as previously reported. The product mixture can be classified in four groups: bicyclic ($C_{10}H_{18}$), monocyclic ($C_{10}H_{20}$), aromatic ($C_{10}H_{14}$) and unsaturated ($C_{10}H_{16}$) compounds. The conversion and selectivity of each group is depicted in Table 6. The dehydrogenation of a cyclohexane ring to an aromatic ring is a rapid reaction and is probably in equilibrium. Consequently, the hydrogenated monocyclic must be compounds that cannot undergo a direct dehydrogenation such as 1,1,2,3- and 1,1,2,5-tetramethylcyclohexanes (see Scheme 9 on p. 45). These compounds can further react to an aromatic compound only after demethylation, producing 1,2,3- and 1,2,4-trimethylbenzenes [128]. Small amounts of alkylcyclopentanes from the hydrogenolysis of camphanic and fenchanic compounds are also observed in this group. Bicyclic compounds are the hydrogenated form of all possible camphenic and fenchenic isomers (Scheme 9). There are three possible saturated isomers from camphenic compounds and six from fenchenic compounds and after reaction all nine are present in the product distribution. Aromatic compounds consist essentially of p-cymene excepted for some cases where m-cymene and o-cymene appear. It can be concluded that monocyclic compounds are a result of the hydrogenolysis function of the catalyst, bicyclic compounds of the intra-ring
isomerization function, and aromatic compounds of the ring opening isomerization function (see Scheme 9 on p. 45).

From Table 6 it is clear that thermal fission is not a dominant reaction as the conversion of \(\alpha\)-pinene without catalyst is only ca. 10%. Furthermore, the absence of Pd on the support completely eliminates the hydrogenation/dehydrogenation function of the catalyst and unsaturated terpenes are preponderant. The isomerization function is then the only function remaining, converting all \(\alpha\)-pinene into camphenic, fenchenic and p-menthadienic compounds. Upon addition of Pd no unsaturated compounds remain and only hydrogenated and aromatic compounds are formed. The existence of unsaturated single bonds as in camphene and fenchene is thermodynamically unfavorable under reductive conditions at a temperature of 300°C. It is therefore important to notice that, once a component has been saturated with hydrogen, it is considered to be a stable end product, which does not undergo further reactions (one exception is pinane see Table 7).

**Table 7: characteristic compounds in the two main group of products from Table 6**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reactants</th>
<th>Distribution of aromatics (%)</th>
<th>Distribution of bicyclics (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>p-Cymene</strong></td>
<td><strong>Others</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Pinanes</strong></td>
<td><strong>Isocamphanes</strong></td>
</tr>
<tr>
<td>Pd/D-11-10 α-Pinene</td>
<td>99</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Pd/D-10-10 α-Pinene</td>
<td>98</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Pd/Carbon α-Pinene</td>
<td>92</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>Pd/D-11-10 Pinane</td>
<td>99</td>
<td>1</td>
<td>---</td>
</tr>
<tr>
<td>Pd/Carbon Pinane</td>
<td>96</td>
<td>4</td>
<td>---</td>
</tr>
<tr>
<td>Pd/D-11-10 Camphene</td>
<td>97</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Pd/Carbon Camphene</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* see text, ** mostly fenchanic compounds, nd: not determined

The product distribution within the aromatic and bicyclic compounds shows the degree of isomerization that has occurred before the different compounds are saturated (Table 7). The following can be concluded when correlating the reactivity of \(\alpha\)-pinene, pinane, and camphene with the catalyst functions (Table 6 and Table 7):

1. Over mildly acidic catalysts such as Pd/-D11-10 and Pd/D-10-10, p-cymene forms rapidly and in good yields. There is also a wide distribution of camphanic and fenchanic by-products (bicyclic compounds), that hardly vary upon an increase of the WHSV. These products can be considered as stable end-products.
2. Pd/carbon is considered to be non-acidic. However, some isomerization activity remains but only lower amounts of fenchanic compounds are formed. When α-pinene is used with Pd/carbon, the proportion of bicyclic compounds is amplified from the important part of pinane that comes up from simple hydrogenation. The isomerization is probably caused from residual acidity remaining on the catalyst and not from a metal catalyzed mechanism. Contrary to Pt, pure metallic Pd is very inactive for isomerization [129].

3. Pd/carbon seems to have a higher hydrogenolysis activity than Pd/D-11-10. However, the hydrogenolysis activity increases due to a decrease in the isomerization activity so that hydrogenolysis has more time to occur on the cyclobutane ring.

4. Pinane is less reactive than α-pinene but still produces more p-cymene than camphene on an acidic catalyst. It isomerizes predominantly to camphanic compounds. The tension in the cyclobutane ring is of course the reason for this behavior. On Pd/carbon the conversion is low and the dominant reaction is the hydrogenolysis.

5. Camphene is less selective to p-cymene than α-pinene and acid sites are required to form p-cymene in significant amounts. The results show that only the acid sites are responsible for the C-C bond cleavage of the camphenic structure. Hydrogenolysis occurs almost exclusively on a four membered ring (α-pinene and pinane), producing 1,1,2,3- and 1,1,2,5-tetramethylcyclohexanes. Only minor amounts of alklycyclopentanes are observed.

The effect of the temperature on the relative rate of the different type of reactions is presented in Figure 9. At low temperatures the formation of bicyclic compounds prevails, whereas an initial increase in temperature favors p-cymene. The dominant reaction at low temperatures is the isomerization of α-pinene to camphanic compounds followed by hydrogenation in agreement with Stanislaus and Yeddanapalli [116]. In contrast, hydrogenolysis becomes dominant at high temperatures and a maximum in the formation of p-cymene is attained at around 300°C. The result is consistent to the fact that hydrogenolysis is a very demanding reaction requiring high temperatures [69]. It is also noticed a small increase of monocyclic compounds at 200°C attributed to the formation of p-menthane.
1.4. Reaction mechanism

Following the conclusions in the last paragraph a reaction mechanism is proposed for the conversion of α-pinene over a weakly acidic Pd supported silica catalysts under a reductive atmosphere as depicted in Scheme 9. In a first step, α-pinene is very rapidly isomerized to p-menthadienic and camphenic compounds in ca. 60% and 40% yields, respectively. Before the dehydrogenation takes place the isomerization has probably reached the equilibrium mixture of p-menthadienic, camphenic and fenchenic compounds. The values in brackets in Scheme 9 indicate the isomeric equilibrium composition for the individual compounds in each group as published elsewhere [130,131]. In a second step, the p-menthadienic compounds dehydrogenate to p-cymene and the camphenic and fenchenic compounds hydrogenate to their respective saturated compounds which can be considered more or less as stable end-products. The side reaction, hydrogenolysis, produces 1,1,2,5- and 1,1,2,3-tetramethylcyclohexanes and small amounts of alkylcyclopentanes. The first two compounds can be further dehydrogenated to 1,2,3- and 1,2,4-trimethylbenzenes.
Scheme 9: the proposed reaction mechanism for the transformation of α-pinene under the typical dehydrogenation conditions
The hydrogenation of single unsaturated bonds as present in α-pinene is usually a rapid reaction, but in this case it is probably slower than isomerization. If the product distribution obtained from the conversion of α-pinene is compared to the product distribution obtained from the conversion of camphene an almost identical GC spectrum is obtained (Figure 10). The difference lies in the peak intensity of p-cymene and hydrogenated bicyclic compounds. For camphene there is a strong increase in the amounts of hydrogenated bicyclic compounds at the cost of p-cymene whereas the opposite is true for α-pinene. Although it is difficult to
determine which bicyclic compound is exactly what product in the GC-MS, the identical product distribution can be seen as a GC fingerprint for camphanic and fenchanic compounds. It clearly shows that part (40%) of the \( \alpha \)-pinene is very rapidly isomerized to camphenic compounds before hydrogenation. This aspect is the opposite of what is usually observed in catalytic reforming [8]. The high energetic level of terpenes and especially \( \alpha \)-pinene with the cyclobutane ring favors very rapid isomerization at the cost of hydrogenation/dehydrogenation.

Another aspect which has not been reported yet is the determination of the fenchanic compounds. The isomerization of camphene can produce two other compounds, namely tricyclene and bornylene. The formation of fenchenic species means that a methyl shift has occurred from skeletal isomerization. The industrial reactions for the production of camphene from \( \alpha \)-pinene are commonly performed in the liquid phase at relatively mild temperatures, which maximize the formation of camphene, tricyclene and bornylene. In our case, however, the reaction temperature is 300°C and the energy input is therefore substantially higher favoring skeletal isomerization. From such a mechanism some other bicyclic compounds can also be generated as illustrated in Scheme 9.

The formation of fenchenic species as intermediates is further ascertained by analyzing the product distribution upon the use of camphene as reactant. In the aromatic fraction, some m-cymene is detected which would be expected if fenchenic compounds are used [Table 7]. The presence of m-cymene in the product distribution of camphene shows therefore that a secondary ring opening reaction occurs when fenchenic compounds are formed from the isomerization of camphene. m-Cymene is not detected when \( \alpha \)-pinene is used due to the lower camphene concentration which arises.

One would expect that stronger acid sites will promote the ring opening reactions of \( \alpha \)-pinene and camphene [121,122,132]. We have shown however that zeolites have too strong acid sites and that an optimal acidity is obtained with supports based on \( \gamma \)-alumina (D-10-10) and silica (D-11-10). On low acidic catalysts such as Pd/carbon there is still some isomerization, but the product distribution is quite different, with less bicyclic compounds being produced and the formation of isocamphanes being predominant. Figure 10 shows the bicyclic compound distribution for both catalysts (Pd/D-10-10 and Pd/D-11-10) upon reaction of \( \alpha \)-pinene. The
distribution is quite similar for both catalysts with Pd/D-10-10 having slightly more isomers. From this result it can be concluded that an equilibrium mixture is obtained on both catalysts. The hydrogenated products originate from the equilibrium mixture of unsaturated camphenic and fenchenic compounds as denoted in Scheme 9.

1.5. Role of hydrogen and deactivation

From the reaction mechanism proposed in this work, it is clear that the camphenic compounds are saturated with hydrogen, preventing them to react further to p-cymene. Hydrogen has then an ambiguous role as also revealed in Figure 11

When hydrogen is replaced with nitrogen using the same reaction conditions, the initial p-cymene yield is higher, but a progressive deactivation is also observed: within 1 h the yield of p-cymene becomes lower than under hydrogen conditions. The catalyst activity is stabilized by the presence of hydrogen and the Pd/D-11-10 catalyst does not seem to deactivate within this period of TOS. This is however not the case with Pd/D-10-10 which slowly deactivates even in the presence of hydrogen.
Thermogravimetric analysis is used for the identification of carbonaceous deposits (Figure 12) In the mass loss derivative (DTG) for a Pd/D-11-10 used in the presence of hydrogen only a small hump is found at 190°C when compared to the starting material which is only subjected to the standard reduction. If the catalyst is operated with nitrogen as the carrier gas, this hump becomes however an intense peak. From the large amount of heat evolved (DSC), this peak is attributed to the oxidation of coke which is in intimate contact with Pd; Pd catalyzes the oxidation. A second intense peak is found for Pd/D-10-10, which is probably a result from coke on the carrier instead of on the Pd particles. Indeed the temperature (500°C) at which this peak occurs is typical of carbon thermally burning.

The first type of coke related to Pd is very quickly formed during the first minute of TOS and its intensity increased only to a minor extent at longer TOS. This shows that without hydrogen the surface free energy of the metal is rapidly reduced by carbonization and a complete surface coverage of a metal-carbide is probably involved. These carbon fragments can afterwards polymerize and form a graphite-like structure. This polymerization is a slower process than the carbonization and can explain the slow increase in peak intensity after the first minutes of TOS. The presence of hydrogen reduces considerably the carbonization process as hydrogen forms similar surface metal-hydride species which are in direct
competition for the adsorption sites. This competition is a direct function of the hydrogen partial pressure, leaving part of the metal surface free of carbon and available for the reaction.

The second type of coke, related to the carrier, is attributed to coke formed on stronger acid sites as present on γ-alumina. The p-menthadienic compounds are probably the intermediates in the formation of these heavy compounds as is the case during the isomerization of α-pinene [124]. These diolefins with a C$_6$ carbon ring polymerize rapidly to a highly aromatic coke which is not very labile. The constant deactivation of Pd/D-10-10 observed in Figure 11 is likely caused by a steadily amount of coke growing on the acid sites during the whole reaction time. It is not detected on Pd/D-11-10 which carrier has weaker acid sites. It can than be concluded that Pd/D-11-10 is the most appropriate catalyst for the present reaction.

The rate of coke formation is a balance between hydrogen pressure, reaction temperature, and feed composition. In the absence of hydrogen the metal surface is completely covered with carbon whereas with increasing hydrogen pressure, the metal surface becomes partially cleaned of carbonaceous residues. At high pressure, the deactivation is very low but the formation of aromatic compounds is incomplete. For catalytic reforming of petroleum naphtha a good compromise with a Pt/alumina catalyst at 480°C is a hydrogen pressure of 20 bar [69]. In our case the reaction temperature is only 300°C as a result the hydrogen pressure can be substantially reduced down to atmospheric pressure.

### 1.6. Crude sulfate turpentine as reactant

The two major components of the crude sulfate turpentine (CST) investigated in this work are α-pinene (65 wt%) and β-pinene (25 wt%). The sulfur content is evaluated at 0.8 wt%, making a direct use of this turpentine unthinkable with a noble metal catalyst. Moreover, CST from a Kraft paper mill contains also some fatty acids and gum resin. Hence a cleaning treatment, consisting of a washing treatment with an aqueous solution of NaOCl (5 wt%) for the reduction of the sulfur content and a distillation for the removal of heavy products is performed. After this treatment the CST acquired a pale yellow color contrary to the initial dark brown color, and the sulfur contain is reduced by 90% to 0.1 wt%.
Although the major part of the sulfur is removed, Pd/D-11-10 still suffers from a serious drop in activity (Figure 13). If ZnO particles are added upstream of the catalyst packed bed the system shows a stable activity for the first 30 minutes. As soon as the ZnO is saturated with sulfur a decrease in the activity comparable to the system without ZnO occurs, and a characteristic H₂S smell is then perceptible in the products. The result shows that it is possible to obtain a similar p-cymene yield starting from CST as with α-pinene. The reactivity of β-pinene can be considered to be very similar to that of α-pinene. The deactivation by sulfur remains an important drawback that must be met by more efficient but unfortunately also more expensive desulfurization methods.

Figure 13: yield of p-cymene from CST as a function of TOS on the most efficient catalyst (T = 300°C, P = 1.01 bar, WHSV = 6 h⁻¹, terpenes/H₂ molar ratio = 4, catalyst weight = 1 g)

1.7. Conclusion

The reaction is a nice example of catalytic dual-functionality for the transformation of chemicals from natural sources. The reaction is to some extent comparable to catalytic reforming but owing to the fact that natural products have an intrinsic higher energy level than saturated paraffins, the reactivity is somewhat different. Thus, isomerization becomes the
fastest reaction and hydrogenation/dehydrogenation the rate determining step. The catalyst acidity is also better reduced and the conventional γ-alumina used for catalytic reforming is replaced by silica with weaker acid sites to carry out the isomerization. The appearance of fenchanic compounds is an indication that at 300°C the silica based catalyst is also capable of skeletal isomerization. Carbonaceous deposit is a major concern for the following reaction due to p-mentadienic compounds that occur as intermediate and can readily oligomerize. Thus, the coke content is substantially reduced by the use of silica. Nevertheless, side reactions such as hydrogenolysis still remain an undesired reaction which significantly reduces the yield.

The use of CST shows that the same yield is obtained starting from the crude material. β-pinene which composes up to 25% the CST has the same reactivity than α-pinene and is not an hindrance for the present reaction. The presence of sulfuric compounds is however a major drawback and further desulfurization investigations with more appropriate oxidation agents are required.
2. ALKYLATION OF BIPHENYL AND NAPHTHALENE

The catalyst of choice for the synthesis of linear molecules such as 4,4'-diisopropylbiphenyl (4,4'-DIPB) and 2,6-diisopropynaphthalene (2,6-DIPN) is a dealuminated zeolite mordenite. Companies like Kureha, NKK, Chiyoda or DOW Chemicals are now on pilot plant developments for these technologies [1]. The number of companies involved is still relatively modest when compared to the important economical significance of these linear products. These companies hold of course the patent rights and prevent further utilization of zeolites with a mordenite structure. Thus, there is a great interest to develop new catalytic systems which uses different zeolite structures. Zeolite beta is a potential candidate because its behavior is still misunderstood in the literature (see prior art). The following work is then intended to study different modifications brought to zeolite beta in order to increase its shape-selective property during the alkylation of biphenyl and naphthalene with propylene. The work will also analyze in details the reactivity of modified beta zeolites in comparison to modified mordenite zeolites.

2.1. Activity of standard materials

The alkylation of biphenyl and naphthalene with propylene by a Friedel-Crafts mechanism produces a mixture of isomers with 4-IPB, 4,4'-DIPB, 2-IPN and 2,6-DIPN as desired components (Scheme 10).

\[
\text{Propylene} \quad \begin{array}{c}
\text{once alkylated (4-IPB)} \\
\text{twice alkylated (4,4'-DIPN)}
\end{array}
\]

\[
\text{Propylene} \quad \begin{array}{c}
\text{once alkylated (2-IPN)} \\
\text{twice alkylated (2,6-DIPN)}
\end{array}
\]

Scheme 10: isopropylation of biphenyl and naphthalene and formation of the most slim isomers

With biphenyl there is a possibility of three isomers for the once alkylated compounds and a possibility of sixteen isomers for the twice alkylated compounds. On the other hand, with
naphthalene, the once alkylated compounds yield two possible isomers while the second alkylated compounds yield twelve possible isomers. Third and higher alkylated compounds are in both cases undesired. Throughout this work, the term PD-1 and PD-2 will refer to the product distribution of once and twice alkylated products and the selectivity of one compound will refer to its relative concentration with the other isomers in the same product distribution.

Figure 14: product distribution in the alkylation of biphenyl with propylene over commercial standard materials (T = 250°C, P = 10 bar, t = 3 h, BP = 20 g and catalyst = 0.5 g)

The catalytic behavior of typical commercial zeolites (H-BEA-std and H-MOR-std), silica-alumina (SA), γ-alumina and silica is shown in Figure 14. These catalysts will afterwards become the non-modified standard reference materials. The reactions were performed in a three-phase slurry reactor by maintaining a constant propylene pressure (10 bar) throughout the reaction time over the reacting medium (biphenyl, catalyst and soluble propylene). In this work, SA is the most active material and it forms rapidly three and more substituted products. These molecules are very bulky and as expected no shape selectivity is associated with this catalyst. The unique characteristic of zeolites for cracking reactions over amorphous silica-aluminas is the increase of acid site density [69]. It is therefore surprising to notice that SA is the most active catalyst for the alkylation. Mass transfer limitations must likely account for the differences observed. This effect is predominant on H-MOR-std, which has a one dimensional pore structure, but also detected on H-BEA-std. H-MOR-std highly favors the
formation of PD-2 products even at a relatively high conversion while H-BEA-std has an intermediate position between SA and H-MOR-std. This unique property of zeolite mordenite is of course inferred to its shape-selective capacity. Pure silica is completely inactive for the reaction while γ-alumina possesses an activity that is not negligible. It is to note that exactly the same behavior is also observed for the alkylation of naphthalene.

2.2. Modifications brought to zeolite beta

There exist many possible modifications that can be applied to a zeolite in order to change its reactivity. The methods studied in this work include steaming, high temperature calcination, acid leaching, SiCl₄ treatment, cation exchange, and isomorphous aluminum substitution. A purely empirical catalyst screening is chosen to preliminary identify a favorable method. Part of the catalysts were prepared from my predecessor [133] and directly tested for the isopropylation reactions. The results concerning acid leaching, steaming and high temperature calcination are presented in Figure 15 in comparison to the results obtained over the standard unmodified beta zeolite (H-BEA-std).

![Figure 15: catalyst screening of the modified beta zeolites in the alkylation of biphenyl with propylene](T = 250°C, P = 10 bar, t = 6 h, BP = 20 g and catalyst = 0.8 g)
The selectivities (to 4-IPB in PD-1 and 4,4’-DIPB in PD-2) obtained over H-BEA-std are similar to the selectivities obtained over silica-alumina (vide infra). Contrary to the dealumination of zeolite mordenite, the dealumination of zeolite beta does not bring a sharp increase in selectivities. The results can be properly compared because the conversion remains high for all catalysts (C > 85%). The only slight increase in selectivities occurs with H-BEA, 1 HCl. All other catalysts have selectivities comparable or lower than the standard reference zeolite. In fact, between all the dealumination procedures studied in this work only acid leaching gives an increase of selectivities. This preliminary result lead us to study the influence of dealumination by acid leaching in more deep.

2.3. Dealumination by acid leaching

Zeolite beta has a less stable structure than zeolite mordenite and readily dealuminates even with mild acid solutions [133]. In Table 8 it is seen that a 1 M HCl concentration already dealuminates the standard beta zeolite to a SiO_2/Al_2O_3 ratio of 202. Further treatments with a 6 M HNO_3 solution leads to a module of more than 1000. It is difficult to further dealuminate zeolite beta once a module of 1000 is attained and the remaining aluminum seems to be tightly bond to the structure. On the other hand, when submitted to the same treatments less dealumination is observed for zeolite mordenite while complete dealumination is observed for silica-alumina.

<table>
<thead>
<tr>
<th>Catalysts / treatments*</th>
<th>Std SiO_2/Al_2O_3</th>
<th>1 M HCl SiO_2/Al_2O_3</th>
<th>6 M HNO_3 SiO_2/Al_2O_3</th>
<th>2 x 6 M HNO_3 SiO_2/Al_2O_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA</td>
<td>25</td>
<td>202</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>H-MOR</td>
<td>22</td>
<td>80</td>
<td>240</td>
<td>400</td>
</tr>
<tr>
<td>Silica-alumina</td>
<td>11</td>
<td>620</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* acid leaching overnight (16 h) followed by a standard calcination, modules determined by ICP

The influence of the acid leaching on the catalytic activity and selectivities of the standard beta and mordenite zeolites in the isopropylation of biphenyl is depicted in Figure 16. As the SiO_2/Al_2O_3 ratio increases the selectivities to 4-IPB and 4,4’-DIPB increase too. Zeolite mordenite shows the typical behavior observed in the literature i.e. a maximum in the
catalytic activity at a SiO$_2$/Al$_2$O$_3$ ratio of ca. 25-30. The reasons of this behavior have already been mentioned in the prior art. In contrary, the conversion over zeolite beta decreases gradually with dealumination. As will be shown later, the formation of a new mesopores does not take place within this zeolite and only the decrease in acid site density accounts for the reduction in activity. In addition, it is not possible to increase the selectivity with further dealumination and the results indicate that a maximum is attained with a 6 M HNO$_3$ treatment.

<table>
<thead>
<tr>
<th>Conversion (mordenite)</th>
<th>Conversion (beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity to 4-IPB in PD-1</td>
<td>Selectivity to 4-IPB in PD-1</td>
</tr>
<tr>
<td>Selectivity to 4,4'-DIPB in PD-2</td>
<td>Selectivity to 4,4'-DIPB in PD-2</td>
</tr>
</tbody>
</table>

Figure 16: influence of the module on the conversion and selectivities of mordenite and beta zeolites for the isopropylation of biphenyl (T = 250°C, P = 10 bar, t = 3 h, BP = 20 g and catalyst = 0.5 g)

It is still not possible to conclude of shape selectivity unless the selectivities are compared under similar conversions. Figure 17 shows the selectivities of the optimal beta catalyst (H-BEA-HNO$_3$) compared to the standard material (H-BEA-std) as a function of the conversion for the alkylation of biphenyl. A clear increase in selectivities is observed for H-BEA-HNO$_3$ in comparison to H-BEA-std for the formation of 4-IPB and 4,4'-DIPB. The gain in selectivities between both zeolites at zero conversion is ca. 14% for 4-IPB and ca. 15% for 4,4'-DIPB. When compared to the single-point results of silica-alumina at 41% conversion, it appears that even the standard beta zeolite is to some extent shape-selective for the formation of 4,4'-DIPB. In all cases the selectivities decrease regularly with the conversion indicating isomerization to more stable compounds (see prior art). The slopes for
H-BEA-HNO₃ are slightly lower than for H-BEA-std which indicate that isomerization is reduced after the acid treatment. Similarly, the isomerization of 4-IPB seems to proceed slightly faster than the isomerization of 4,4'-DIPB on both catalysts.

Figure 17: the selectivities as a function of the conversion in the alkylation of biphenyl with propylene
(T = 250°C, P = 10 bar, from various experiments)

Figure 18: the selectivities as a function of the conversion in the alkylation of naphthalene with propylene (T = 200°C, P = 10 bar, from various experiments)
The importance to compare selectivities under similar conversions is demonstrated in Figure 18 which shows the results concerning the alkylation of naphthalene. It is seen that the selectivities to 2-IPN and 2,6-IPN can be fitted by two single curves for the three catalysts studied. Thus, it is not possible to improve the selectivities with an acid treatment of zeolite beta for this reaction. For 2-IPN, the selectivity decreases rapidly at low conversions while for 2,6-DIPN the selectivity is relatively constant throughout the conversions. The behavior for 2-IPN is surprising because one would expect that isomerization increases its concentration at higher conversions, however, the reverse behavior is observed. No explanation could yet account for this phenomenon.

It can now be concluded that zeolite beta is intrinsically a shape-selective catalyst for the alkylation of biphenyl with propylene. Nevertheless, the increase in total yield of 4,4’-DIPB for an acid treated zeolite beta remains modest in comparison to a dealuminated zeolite mordenite. For the alkylation of naphthalene with propylene no shape selectivity is observed and the results over silica-alumina, H-BEA-std, and H-BEA-HNO₃ are all comparable.

### 2.4. Influence of the temperature

The influence of the temperature can give an indication on the type of shape selectivity involved in the reaction (see prior art). In Figure 19 an increase in the selectivities to the most slim isomers is observed with the increase of the temperature which indicates that a product selectivity is likely to occur on H-BEA-HNO₃. The dotted lines in the figure represent a correction for results that would be expected at equal conversions without the influence of isomerization (from Figure 17). In these particular cases, the trend toward a product selectivity is even amplified. There is, however, an upper limit to further increase the temperature which is dictated by deactivation due to coke formation. The next section will show that at 250°C the deactivation is important.
2.5. Catalytic activity, deactivation and coke formation

The activity of a zeolite catalyst in organic reactions cannot be treated separately from deactivation due to coke formation which is always present during cracking, alkylation or isomerization [8]. Figure 20 shows the kinetic profile of the alkylation reaction for the standard and the HNO₃-treated catalysts at 250°C. The non-dealuminated catalyst is the most active. This behavior is expected as long as no new mesopores are created. The activity is then only a function of the Brönsted acid site density which can be determined for example by pyridine adsorption and FTIR. However, due to mass transfer limitations a non-linear behavior is foreseen (vide infra). Moreover, the occurrence of deactivation is deduced from the shape of both curves in Figure 20 because the curves tend to reach a plateau before complete conversion. This trend is quite obvious on H-BEA-HNO₃.
Figure 20: catalytic activity of isopropylation of biphenyl as a function of reaction time \((T = 250^\circ C, \ P = 10 \text{ bar}, \ BP = 50 \text{ g and catalyst } = 1.25 \text{ g})\)

Alkylation reactions follow usually an Eley-Rideal mechanism (1) where one species is strongly adsorbed on the acid sites and attacked by the second nucleophilic species to create an adsorbed complex (the Wheland intermediate in Scheme 4):

\[
-r = k\theta p C_{BP} = \frac{k K_p C_p C_{BP}}{1 + K_p C_p + K_{BP} C_{BP} + K_{BP^2} C_{BP^2}} = \frac{k K_p C_p C_{BP}}{1 + K_p C_p} = k_{app} C_{BP} \quad (1, 2, 3, 4)
\]

In equation (1) \(k\) represents the specific reaction rate, \(\theta p\) the fractional surface coverage of propylene, and \(C_{BP}\) the concentration of biphenyl in the reaction mixture. If one performs the typical substitution by assuming Langmuir adsorption isotherms equation (2) is obtained. In this equation the possible adsorption of biphenyl (\(K_{BP} C_{BP}\)) and products (\(K_{IPB_s} C_{IPB_s}\)) on the active sites is accounted. However, in our conditions the pressure of propylene is high enough to cover most of the Brönsted acid sites as isopropyl cation. The group of Sugy et al. [96] demonstrated this behavior and they furthermore determined that this preferential adsorption of propylene on the acid sites considerably limited the isomerization of the products by blocking the reaction intermediate (the arenium cation as depicted in Scheme 6). Thus the terms \(K_{BP} C_{BP}\) and \(K_{IPB_s} C_{IPB_s}\) can be neglected in equation (2) leading to equation (3). Finally,
the propylene concentration is constant throughout the reaction and by assuming that its relative solubility in the liquid is constant too, the terms $K_p C_p$ remains invariable. It is then possible to include all the constant terms in one general constant ($k_{app}$) which typically means an apparent reaction rate. Thus, the general equation (1) is transformed to a pseudo-first order equation (4). Moreover, due to mass transfer limitations, $k_{app}$ must definitely be seen as an apparent reaction rate (vide infra).

Deactivation is a complex phenomenon and is usually mathematically described by empirical equations [134]. The activity decline ($a$) is usually described by zero, first or second order (5) expressions. By combining the integrated expression of a second order deactivation (6) with the pseudo-first order equation (4), one obtains after integration a mathematical model of the slurry batch alkylation reactor (7):

$$
\frac{-da}{dt} = k_D a^2 ; \quad \frac{1}{a} = 1 + k_p t ; \quad x = 1 - \left[ \frac{1}{(1 + k_p t)^{k_{app}/k_D}} \right]
$$

The expression represents the design equation for a batch reactor with a second order deactivation. The terms ($x$) and ($t$) represent the conversion and reaction time and the factor ($k_D$) the deactivation constant. The integrated model is of course an oversimplification of the actual reaction mechanism but it is well suited to approximate the experimental data of Figure 20. It is intended to understand the general behavior in a qualitative way. When no deactivation is used in the model it is not possible to fit the experimental data which shows that deactivation is an important aspect of the reaction. Moreover, the second order deactivation expression (5) is the most appropriate deactivation model which gives the best experimental fit (minimal least-square errors). The results are shown in Figure 20 by the two interpolating curves and a quite good fit is observed for all the experimental points.

The parameters $k_{app}$ and $k_D$ for the two catalysts can now be extracted and the values are reported in Table 9. The table shows also the relative Brönsted acidity of both catalysts as well as their corresponding $k_{app}/k_{app}$ and Brönsted/Brönsted (B/B) ratio values. The values of $k_{app}$ represent the initial catalytic activity. The values can also be determined graphically by the initial slope of the curve at $t = 0$ min. Both methods have been used and a deviation of less than 5% has been found which shows the consistency of the model at least at low
conversions. Alkylation with alkenes is a typical Brönsted acid catalyzed reaction (see prior art). The catalytic activity should be function of the number of Brönsted acid sites. However, from Table 9 one can see that it is not the case; the increase in catalytic activity from H-BEA-HNO₃ to H-BEA-std (ratio \( k_{app}/k_{app} \)) is lower than the increase in the number of Brönsted acid sites (ratio B/B) which suggest that the reaction is mass transfer limited.

Table 9: value of the constants in equation (7) and relation to the catalyst Brönsted acidity

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( k_{app} )</th>
<th>( k_D )</th>
<th>Brönsted intensity*</th>
<th>Ratio ( k_{app}/k_{app} )</th>
<th>Ratio B/B**</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA-std</td>
<td>0.098</td>
<td>0.12</td>
<td>100</td>
<td>5.2</td>
<td>12</td>
</tr>
<tr>
<td>H-BEA-HNO₃</td>
<td>0.019</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* relative values determined from pyridine adsorption FTIR, ** ratio of Brönsted intensities

By definition the effectiveness factor (8) represents the actual overall reaction rate (\( r_1 \) or \( r_2 \) where subscript 1 stands for H-BEA-std and subscript 2 for H-BEA-HNO₃) divided by the intrinsic rate that would occur in the absence of diffusion (\( r_{11} \) or \( r_{12} \)):

\[
\eta_1 = \frac{r_1}{r_{11}} \quad \text{or} \quad \eta_2 = \frac{r_2}{r_{12}} \quad ; \quad \frac{r_{11}}{r_{12}} = 12 \quad ; \quad \frac{\eta_1}{\eta_2} = \frac{r_1}{12r_2} \quad (8, 9, 10)
\]

The relation between \( r_{11} \) and \( r_{12} \) is the difference in their number of Brönsted acid sites namely a factor 12 as expressed in equation (9). With the appropriate substitution and a division of the effectiveness factors relation (10) is obtained. The Thiele modulus (\( \phi \)) is a measure of the ratio of surface reaction rate to the rate of diffusion through the catalyst micropores:

\[
\phi_1^2 = \frac{r_c^2 r_{11}}{D_{eff} C_s} \quad \text{or} \quad \phi_2^2 = \frac{r_c^2 r_{12}}{D_{eff} C_s} \quad ; \quad \frac{\phi_1}{\phi_2} = \frac{\sqrt{r_{11}}}{\sqrt{r_{12}}} = \sqrt{12} \quad ; \quad \eta_1 = \frac{3}{\phi_1} \quad \text{or} \quad \eta_2 = \frac{3}{\phi_2} \quad (11, 12, 13)
\]

When the Thiele modulus is large (\( \phi > 1 \) for first order reaction), diffusion limits the overall reaction rate. If we presume that on both catalysts (H-BEA-std and H-BEA-HNO₃) the morphology of single crystallites is not significantly changed after the acid treatment (vide infra) than the crystallite radius (\( r_c \)), the effective diffusivity (\( D_{eff} \)) and the surface reactant concentration (\( C_s \)) remain the same. Only the intrinsic reaction rates change in the expression
of the ratio of the Thiele modulus and by combining them with relation (9) one obtains a single factor of 3.5 (12). A relation between the effectiveness factor and the Thiele Modulus exist for first order reactions which can be reduced to the simple expression (13) for large Thiele modulus ($\phi > 30$) [134]. A large Thiele modulus would be expected in configurational diffusion of bulky molecules in micropores. It is now possible to enter the factor $\eta_1$ and $\eta_2$ from equation (13) into expression (10) and by the use of the result in (12) the general following relation is found:

$$r_1 = \frac{12r_2}{\sqrt{12}} = \sqrt{12}r_2 = 3.5r_2$$

(14)

This proportional factor (3.5) represents the theoretical gain in activity that would be expected if the reaction is highly mass transfer limited. On the other side, is the factor 12 (ratio $B/B$, Table 9) which would be expected without any mass transfer limitations. The experimental value of 5.2 ($k_{app}/k_{app}$, Table 9) is relatively close to 3.5 in comparison to 12 so that it can be concluded that the alkylation of biphenyl with propylene on zeolite beta is a highly mass transfer limited reaction.

Another interesting aspect of Table 9 is the values of the deactivation constant ($k_D$). The values on both catalysts are quite similar which suggests that both catalysts deactivate at the same rate. It would mean that the dealumination procedure by acid leaching does not conduct to a more durable catalyst. This observation is in disagreement to what is usually noticed on zeolite mordenite [77]. The nature of coke species on the catalyst after reaction can be deduced from the profile of the DTG curves in Figure 21. For H-BEA-std, one major peak is observed at about 510°C. This peak is attributed to the thermal oxidation of heavy polymeric and aromatic species [77]. For H-BEA-HNO$_3$, the peak at a lower temperature (340°C) is as intense as the peak at a higher temperature. It has been attributed for zeolite mordenite to reactants and products entrapped in the micropores [77]. The decrease in the intensity of the high temperature peak accounted for the better stability of zeolite mordenite after dealumination.

One would expect to make the same conclusion for zeolite beta based only on Figure 21. However, the use of a deactivation model (7) shows that this interpretation is likely incorrect. For homogeneous catalysts, the acid sites are always in close relation with coke or coke
precursors [60]. For example, in the alkylation of benzene with propylene with a HCl-AlCl₃ catalyst, deactivation occurs by the formation of organic complexes with the catalyst producing a tarry mixture with the consequence that catalyst regeneration is not possible. The complexes are due to polyalkylated benzenes bonded to HCl-AlCl₃. By analogy, why should it be different with heterogeneous catalysts? Coke molecules have an increased basicity due to the possible delocalization of the positive charge over a large number of aromatic nucleus and they would naturally remain in close relation to the surface acid sites.

![Figure 21: thermogravimetric analysis of the standard and the HNO₃-treated beta zeolites after a typical reaction run (TG is viewed in the mass loss derivative mode (DTG))](image)

From TG measurements, it is then worth to evaluate a coke per acid site concentration factor. The deconvolution of the high temperature peak followed by integration leads to a percentage of heavy products (coke) on the catalyst. Coke(s) are usually undefined heavy aromatic molecules so that a mole percentage is not directly calculable. Nevertheless, it is possible to transform this value to a mole percentage of benzene which can be divided by the number of acid sites (from pyridine adsorption). For H-BEA-std, the value is ca. 3 mol/mol (mol of benzene per mol of acid sites) while for H-BEA-HNO₃ the value is ca. 17 mol/mol. The occupational density of acid sites by coke is quite higher on H-BEA-HNO₃ than on H-BEA-std. Thus, there are no evidences to admit that deactivation is reduced after the acid treatment.
2.7. Structural aspects of zeolite beta

Prior to discuss in details the zeolite characterization it is worth to summarize the structural properties of zeolite beta. Zeolite beta has a three-dimensional network of 12-membered oxygen rings and a void comparable to the faujasite structure. It was first synthesized in 1967 but its structure was only published in 1988 [135,136]. Contrary to zeolite Y it can be directly synthesized with a high and variable SiO$_2$/Al$_2$O$_3$ ratio. Zeolite beta has two comparable straight channels in the a- and b- directions (0.76 × 0.64 nm) and one sinusoidal channel in the c- direction (0.55 × 0.55 nm). The interconnection of these channels forms the three-dimensional pore structure with high accessibility as also suggested by the fully exchangeable charge compensating cations. Zeolite beta does not have inherent supercages but at the intersections of the channels the large empty spaces have a diameter of ca. 1.2 nm which can accommodate large molecules that would not necessarily diffuse through the micropores.

Zeolite beta is build from an intergrown structure of two or three types of polymorphs. The random stacking fault of these polymorphs conducts to a structure that is not well defined in its XRD pattern [137]. Moreover, zeolite beta is characteristic of a substantial concentration of lattice defects from subtle structural disorder [138]. The disorder is believed to create additional Lewis-acid sites mostly located on the internal surface as well as additional cation exchange positions. The typical strong Brønsted acid sites from aluminum tetrahedrally coordinated in the zeolite framework are expected to be on the internal as well as on the external surface. In the later case, the aluminum is however considered to be terminated by a hydroxyl group [138]. The same type of hydroxyl groups is also expected to saturate the aluminum on internal defect sites and depending on the degree of dehydroxylation the aluminum becomes partially uncoordinated developing Lewis acidity. The interchange between Brønsted and Lewis acidity of the aluminum atom still connected to the framework seems to be a characteristic of zeolite beta [139] which is certainly related to its high concentration of structural defects.
2.8. Characterization with nitrogen adsorption, XRD and SEM

It has already been shown that zeolite beta upon acid leaching dealumimates quite faster than zeolite mordenite [Table 8]. The characterization with nitrogen adsorption and XRD of these acid treated zeolites are presented in [Table 10]. The scanning electron microscope (SEM) images are in return presented in Figure 22 and Figure 23 for the beta and mordenite zeolites, respectively.

From Table 10 it is observed that the beta zeolites have a very high external surface area which account for about 38% of the total BET surface area. Alternatively, the mordenite zeolites have a smaller external surface area that remains nevertheless significant. The results can be explained from the tiny primary crystallites that compose the zeolites. In Figure 22 agglomerates of primary beta crystallites are observed which are difficult to separate individually. The size of these primary crystallites is estimated for some particles to be smaller than 20 nm. For the mordenite zeolites, the size of the primary crystallites is roughly 50 nm (Figure 23). Moreover, for the beta zeolites, the mesoporous volume is three times larger than the microporous volume. It indicates the substantial role that can play the mesoporous structure in catalytic reactions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET m²/g</th>
<th>External s. area m²/g</th>
<th>Micro. volume cm³/g</th>
<th>Meso. volume cm³/g</th>
<th>Crystallinity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA-std, HB 99/21</td>
<td>578</td>
<td>214</td>
<td>0.178</td>
<td>0.620</td>
<td>83**</td>
</tr>
<tr>
<td>H-BEA-HCl*, HB 99/64</td>
<td>546</td>
<td>194</td>
<td>0.172</td>
<td>0.652</td>
<td>79</td>
</tr>
<tr>
<td>H-BEA-HNO₃*, HB 99/66</td>
<td>539</td>
<td>188</td>
<td>0.171</td>
<td>0.684</td>
<td>79</td>
</tr>
<tr>
<td>H-MOR-std, HV 95/40</td>
<td>456</td>
<td>82</td>
<td>0.183</td>
<td>0.121</td>
<td>85</td>
</tr>
<tr>
<td>H-MOR-HCl, HB 99/65</td>
<td>464</td>
<td>87</td>
<td>0.185</td>
<td>0.144</td>
<td>96</td>
</tr>
<tr>
<td>H-MOR-HNO₃, HB 99/67</td>
<td>450</td>
<td>84</td>
<td>0.179</td>
<td>0.173</td>
<td>100</td>
</tr>
</tbody>
</table>

* the HCl treatment is with 1 M and the HNO₃ treatment is with 6 M, ** reference material is TEA-BEA-std

The relative crystallinity of the beta zeolites decreases upon the severity of the treatment. The most severe treatment seems however to be the simple calcination to remove the template and the transformation to the H⁺ form where the crystallinity drops from 100% to 83%. In contrast, the situation is reverse for the mordenite zeolites, thereby the crystallinity increases from 85 to 100% with H-MOR-HNO₃ as relative reference. The SEM images clearly show
the presence of a cylindrical impurity phase in the standard material (Figure 23A) which is removed after the HNO$_3$ acid treatment (Figure 23B). The corresponding increase in crystallinity is likely related to this gain in purity. Furthermore, the stability of the microporous volume indicates that strong acid leaching has no real structural effect on the mordenite zeolites besides an increase of the mesoporous volume.

The loss of crystallinity from H-BEA-std to H-BEA-HNO$_3$ is relatively small though it is corroborated from the loss of microporous volume (Table 10). In addition, the effect of acid leaching is also apparent in Figure 22B where a new phase is visible; the roundly spheres with a diameter of ca. 50 nm. Figure 22B does however not represent a statistical distribution of this new phase and from further TEM images its relative concentration can be evaluated at

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**Figure 22: SEM images of the standard and the HNO$_3$-treated beta zeolites**

**Figure 23: SEM images of the standard and the HNO$_3$-treated mordenite zeolites**
around 10 to 20%. It is interesting to note the decrease in external surface area with the increase in average particle diameter after the acid treatment. It can now be concluded that the strong acid leaching procedure with a 6 M HNO$_3$ concentration causes some structural rearrangement though the general integrity of zeolite beta is maintained. More evidences for this statement as well as for the appearance of a new phase will be presented later.

One important aspect of acid leaching is whether or not it creates new mesopores, which considerably reduce the diffusion barrier for mass transfer limited reactions. In our case, there is a slight increase in the mesoporous volume of the beta zeolite (Table 10), nevertheless from the SEM images the morphology of the primary crystallites does not seem to have changed much (with the exemption of these new roundly spheres). It is then not possible to assess a direct influence of acid leaching on the mesoporous structure. It is to recall that the beta zeolite used in this work is a commercial material that is probably already optimized in terms of diffusivity in such a way that its mesoporous volume is already high and its primary crystallites small. The acid leaching of starting materials with quite less mesopores surely conduct to a different conclusion as it is usually observed with zeolite mordenite [86,91].

2.9. Characterization by FTIR spectroscopy

It is possible to recognize distinctively up to seven OH bands for H-BEA-std in the hydroxyl region between 3300-3800 cm$^{-1}$ in Figure 24. The band at 3610 cm$^{-1}$ is commonly referred to the framework bridge OH group which causes strong Brønsted acidity. Terminal silanols are usually expected at around 3740 cm$^{-1}$ though in this work two signals are visible in this range. The most intense peak centered at around 3733 cm$^{-1}$ is attributed to internal silanols and its shoulder at 3742 cm$^{-1}$ to the common external silanols [140]. The inherent high concentration of defect sites in zeolite beta increases the amount of internal silanols, which then become clearly visible in the IR spectrum. These OH groups can also frequently form together hydrogen bonds, which cause the band at 3733 cm$^{-1}$ to tail down to 3300 cm$^{-1}$. The tailing is often considered as a IR band for itself [141]. Moreover, the relative high intensity of the external silanol band compared to the Brønsted acid band is another evidence for the high external surface area and small size of primary crystallites.
The remaining bands more or less visible in Figure 24 for H-BEA-std are caused from aluminum species in different environments. These aluminum species are formed during the template calcination and during the transformation of the zeolite into the $\text{H}^+$ form. Their evolution is a function of the degree and severity of the activation process associated with mechanism such as auto steaming and dehydroxylation. The first type of species expected is aluminum bonded to one or two OH groups but still connected to the framework. The second type of species is likely tiny aluminum cluster detached from the framework in cationic position or as neutral species. Finally, if the activation is severe, polymerization and agglomeration is expected with the formation of large aluminum species. The attribution of the OH bands to these individual aluminum species is still a matter of debate nevertheless many authors have associated the band at 3778 cm$^{-1}$ to small non-charged extra-framework aluminum [141-143]. The band at 3662 cm$^{-1}$ is likely related to OH groups on aluminum that is still connected to the framework [141,143] and the band at 3680 cm$^{-1}$ to OH groups on non-acidic large aluminum clusters [144,145]. In our case for H-BEA-std, the band at 3662 and 3778 cm$^{-1}$ are visible though in weak intensity while the band at 3680 cm$^{-1}$ is a priori not visible but it appears when the zeolite is submitted to physisorbed pyridine (not shown here).

To conclude, it is possible to observe all three possible types of OH groups associated with extra-framework aluminum or to loosely bond framework aluminum. It means that significant
dealumination has taken place even with the careful calcination at 540°C. This aspect is also corroborated from pyridine adsorption which shows that the amount of Lewis acid sites is about equivalent to the amount of Brønsted acid sites (1455 versus 1545 cm⁻¹ bands in Figure 25) indicating that a substantial amount of aluminum is transformed into extra-framework species with Lewis acidic properties.

![Figure 25: FTIR subtraction spectra in the aromatic region of pyridine for the standard and the HNO₃-treated beta zeolites](image)

The acidic strength of the different OH groups can be qualitatively ascertained by employing pyridine adsorption. The result of the OH groups remaining after 16 h evacuation at 150°C to remove all physisorbed pyridine is also presented in Figure 24. It is worth to notice that for H-BEA-std the bands at 3610, 3662 and 3778 cm⁻¹ have been completely removed while the bands at 3742 and 3733 cm⁻¹ have been reduced in intensity. It has already been reported from weak base interaction that the bands associated to AlOH species (3662 and 3778 cm⁻¹) are moderately acidic [140]. On the other hand, the reduction in intensity of the internal and external silanol bands (3733 and 3742 cm⁻¹) could be attributed to an induction effect of the remaining pyridine. However, we firmly believe that these silanol groups are to some extent acidic, an opinion which is also shared by other authors [146,147].

The interest of this work is to analyze the behavior the acid treated zeolites. Heinichen and other authors [144,148,149] showed that moderately concentrated acid solution readily
removed extra-framework aluminum and the corresponding OH bands without significant extraction of the framework aluminum which gives rise to strong Brønsted acidity. In our case for H-BEA-HNO₃ (Figure 24), the band related to strong Brønsted acidity (3610 cm⁻¹) is no more visible and a very broad band has appeared (3300-3724 cm⁻¹) likely related to a substantial amount of new internal silanols in hydrogen bonding; an observation in agreement with previous authors [150]. From this broadening the maximum value of wavenumber for internal silanols has shifted to a lower value (3724 cm⁻¹). Thus, dealumination with strong acid solution has removed a substantial amount of framework aluminum creating silanol nests which are just partially annealed at the typical calcination temperature of 540°C. In addition, it is interesting to notice that the shoulder band for external silanols at 3742 cm⁻¹ is still present in the same intensity as in the parent material. A further proof that strong acid leaching has not significantly damaged the size and morphology of the primary crystallites.

For the acid strength of silanol groups, a substantial difference is observed for H-BEA-HNO₃ after pyridine adsorption and evacuation at 150°C (Figure 24). The total intensity of the broad band is just slightly reduced at the maximum intensity. The internal and external silanol groups cannot be considered as acidic anymore. The dealumination has considerably reduced the acid density of all type of possible acid sites. One could now argue that all the Brønsted acid sites are removed from the acid leaching but from Figure 25 it is seen that the typical band for Brønsted acidity (1545 cm⁻¹) is still present with an intensity 12 times less than on the standard material (Table 9).

We would like to propose the following explanation to account for the weak acidity of silanol groups in zeolites with a high density of defect sites. It is usually accepted that the negative charge of a zeolite is not localized on one tetrahedra but is distributed over the entire framework of oxygen ions [151]. The distribution of negative charges leads to a so-called solvent effect important to stabilize cationic intermediates such as carbocations in the micropores [66]. The density of negative charge is naturally higher close to the aluminum tetrahedra, but if defect sites (additional silanol groups) are in close proximity than the positive charge held by the acid H⁺ cation can be as well distributed, in part, over the defect sites. Thus, a delocalization of positive charges arises comparable to the delocalization of negative charges over the framework of oxygen ions. The consequence is that the acidity of the typical Brønsted acid site is reduced in favor to a small increase of the acidity of the neighboring silanol groups. In a strongly dealuminated zeolite such as H-BEA-HNO₃, the
effect of delocalization is minor so that almost all silanol groups recover their non-acidic character.

2.10. Characterization by $^{29}$Si MAS NMR and $^{27}$Al MAS NMR

The $^{29}$Si NMR spectra of the beta samples for the single-quantum MAS technique are presented in [Figure 26]. In addition to the results with the standard and the acid modified materials, the sodium form of the standard material is also included and in that spectrum two distinct signals are noticeable at -105 and -112 ppm representing the Si(3Si, 1Al) and Si(4Si) signals, respectively. The ion exchange and calcination of this sample to the H$^+$ form (H-BEA-std) decrease the peak intensity at -105 ppm, which indicates that part of the aluminum has migrated out of the zeolite framework as extra-framework aluminum. The acid leaching with strong acid solutions removes a major part of the aluminum but a signal at around -104 ppm is still perceptible.

![Figure 26: single quantum $^{29}$Si MAS NMR spectra of the beta zeolites](image)

The lattice defects (internal silanols) as well as the new silanols created from the dealumination are responsible of this signal and are also the reason why quantitative determination of a framework SiO$_2$/Al$_2$O$_3$ is not possible. The three distinct peaks observed
for the highly dealuminated beta zeolite (H-BEA-HNO₃) at -111, -112 and -115 ppm are a strong indication that the beta structure is still intact after the strong acid leaching. Indeed, the three maximums represent silicon in three groups of different tetrahedral framework positions. These signals are usually only distinguished in high silica material when the line broadening effect of aluminum is considerably reduced [152]. The signals are not as sharp as the signals reported in reference [153] and suggest that a very broad signal from an amorphous material is overlapping the three signals. The same observation was also reported by Liebens et al. [154] for an ultra stable Y zeolite.

There are now enough evidences to stipulate that the new roundly spheres revealed in Figure 22 after the acid treatment come from the formation of an amorphous silica phase. In addition to the NMR spectrum, the size of these new particles is a further indication on the nature of this new phase. Indeed, the size (50 nm) is typical of what is usually encountered in pure silica material such as Aerosil. Moreover, this new phase could account, at least in part, for the very broad IR signal obtained in the hydroxyl region between 3300-3724 cm⁻¹ (Figure 24) and which partly cover the intrinsic signals of the beta zeolite. Such a broad signal is typical for amorphous silica such as Aerosil [155]. A different extinction coefficient is also expected which would account for the very large overlapping signal. The catalytic activity of this phase in acid catalyzed reactions is negligible because residual aluminum in an amorphous phase is very easily leached out (Table 8). If we recall that this phase represent only 10 to 20% of the total and the remaining particles being very similar in diameter and morphology to the non-treated material. So, it can be considered that the intrinsic catalytic property of the beta structure for acid catalyzed reactions is maintained after the 6 M HNO₃ acid treatment.

The corresponding $^{27}$Al MAS NMR spectra are presented in Figure 27. Only one signal is distinguished from the as-synthesized material (TEA-BEA-std) at 55 ppm corresponding to aluminum in tetrahedral position. The calcination of the zeolite to remove the template out of the zeolite structure (Na-BEA-std) brings about the first traces of octahedral aluminum (0 ppm). This trend is even intensified when the zeolite is transformed into the acid form and calcined (H-BEA-std). It is now possible to attribute four types of aluminum signals to the spectrum H-BEA-std. The first one is a large signal at 55 ppm, the second one is a sharp signal at exactly 0 ppm, the third one is the large butt in close connection to the signal at 0 ppm and finally the fourth one is indirectly attributed to the large amount of invisible aluminum that is created (35%). It is common to associate the signals near 0 ppm and the
invisible aluminum to extra-framework aluminum but recently Fajula et al. [144,156] and Kuehl et al. [139] have demonstrated that framework aluminum could be as well octahedral depending of its degree of hydration. From the later reference it is possible to relate the large butt at 0 ppm and probably even the invisible aluminum to tiny extra-framework aluminum clusters in very unspecified environment which explains the very broad signal obtained. Thus, the IR results are confirmed from the $^{27}$Al MAS NMR results and clearly demonstrate that a large number of aluminum atoms are transformed into extra-framework species after calcination and conversion into the H$^+$ form of the standard beta zeolite.

![Figure 27: single quantum $^{27}$Al MAS NMR spectra of the beta zeolites (* for side bands)](image)

The influence of the acid leaching dealumination is also well demonstrated in Figure 27 by the H-BEA-HCl spectrum. There is now only one small sharp signal at 0 ppm and the amount of tetrahedral aluminum corresponds more or less to the amount evaluated by ICP. The extra-framework aluminum has been completely washed off (invisible and broad $^{27}$Al MAS NMR signals) confirming the previous results of Heinichen [133]. The acid leaching with a 1 M HCl has to some extend also attacked the structural aluminum because two signals are now visible at 53 and 57 ppm. It is very fortunate to observe so distinctly two aluminum tetrahedral responses. The acid leaching has removed part of one aluminum species so that the
two signals become optimal in terms of resolution. At this point, it is possible to speculate that the tetrahedral aluminum spectrum is a combination of two signals.

Two-dimensional multi-quantum MAS MNR has been applied to investigate in details this hypothesis. Figure 28 shows that a triple-quantum MAS NMR method (2D-3Q) allows the direct determination of two types of aluminum species in the region of tetracoordinated aluminum. This is true for all the beta zeolites except the non-calcined as-synthesized material. In general the resolution is quite better compared to what is obtained on the same samples by the single-quantum MAS technique. The correct determination of their actual chemical shifts and their quadrupolar parameters are given in Table 11 which gives further structural information about local environment. The effect of acid leaching with concentrated
solutions is now obvious: it removes preferentially one type of aluminum. Over H-BEA-HNO$_3$, the signal at 56.6-58.8 ppm has almost disappeared indicating that this aluminum species is less tightly bonded to the framework.

The question is to know what kinds of aluminum are responsible of the two signals. Pérez-Pariente et al. [153] by analogy to the result with $^{29}$Si MAS NMR deconvoluted a single tetrahedral aluminum component into three signals; each signal related to a different tetrahedral position. Yet, in our case, the quadrupolar parameters of the 2D-3Q MAS NMR experiments (Table 11) indicate that the signal at lower field (56.6-58.8 ppm) has a less symmetrical environment. It suggests that this aluminum species is located in the neighborhood of defect sites.

Table 11: isotropic chemical shifts ($\delta_{iso}$) and quadrupolar parameters for the 2D-3Q $^{27}$Al MAS NMR of the beta zeolites

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{iso}$ (ppm)</th>
<th>SOQE (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA-BEA-std</td>
<td>54.0</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>58.0</td>
<td>1.98</td>
</tr>
<tr>
<td>H-BEA-std</td>
<td>53.6</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>58.2</td>
<td>2.10</td>
</tr>
<tr>
<td>H-BEA-HCl</td>
<td>53.8</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>58.0</td>
<td>1.87</td>
</tr>
<tr>
<td>H-BEA-HNO$_3$</td>
<td>54.6</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>57.0</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Figure 29: single quantum $^{27}$Al CP/MAS NMR spectrum of H-BEA-HCl
\(^{27}\)Al cross polarization (CP) MAS NMR is applied to determine the types of local surrounding the two aluminum species are facing (Figure 29). It is to note that the application of CP to a quadrupolar nucleus such as \(^{27}\)Al is difficult due to the strong loss of signal to noise ratio (see experimental). Nevertheless, the CP results are fortunately unambiguous: the signal which intensify the most during the CP experiments is the one located in the lower field (57 ppm), namely the signal associated with defect sites nearby. It is of course not a stroke of chance, zeolite beta has a high density of lattice defects saturated with OH groups and we now report for the first time a precise determination of these sites when aluminum occupies them.

A simple structure like the one depicted in Scheme 11B could easily account for the aluminum surrounding on the defect site. In that case an Al-OH bond disconnected at that position from the framework replaces one of the Al-O-Si bond. In return, scheme (A) represent the non-perturbed common Brønsted site. Different acid strengths are expected from these two Brønsted acid sites. For example, the possible charge delocalization effect previously introduced would be certainly more dominant on site (B) with a concomitant decrease in acid strength. Thus, site (B) is a kind of perturbed but still strong Brønsted acid site. The illustration of this defect site in Scheme 11B is of course an oversimplification and the real situation is likely more complex. Moreover, structure (B) has also been proposed to terminate the external surface area of a crystallite creating Brønsted acidity on the external surface [138]. In our case the external surface area of the beta zeolites is very high so that acid leaching would inevitably conduct to a passivation of this surface by preferential elimination of these sites. Thus, the intrinsic microporous behavior of zeolite beta would come into effect.

Scheme 11: schematic representation of the two types of aluminum sites in zeolite beta

There are references in the literature that strongly supports the views expressed in this work. For example, Müller et al. [157,158] have investigated in details the dealumination of zeolite beta by \(^1\)H MAS NMR and concluded that two kinds of Brønsted acid sites predominate. The
key point was that zeolite beta showed a large fraction of Brønsted acid sites in interaction with the framework and that the general stability of the zeolite increased when the number of perturbed species decreased. The general view expressed by Maache et al. suggest two types of Brønsted acid sites, one site in areas of high crystallinity and the other in non-well-crystalline areas the later being more extractable by acid leaching [142]. In reference [159] two different Brønsted acid sites are revealed by another independent method namely XPS.

If we look back to Figure 27 and compare the Na-BEA-std and H-BEA-std spectra, the shape of the curve for the acid zeolite indicates that the low field signal has been preferentially reduced. The substantial amount of extra-framework aluminum produced during the calcination to the H\(^+\) form is then mostly provided by the framework aluminum species close to defect sites. Another indication that these sites are less stable. In Figure 25 one can still observe Lewis acid sites for H-BEA-HNO\(_3\) although most of the extra-framework aluminum are absent (Figure 27). The Lewis acid sites remaining are probably due to structural defects produced from the acid leaching. Leaching with concentrated acid solutions directly attack the framework aluminum with the consequence that probably uncoordinated silicon are formed.

### 2.11. Discussion about shape selectivity in zeolite beta

The characterization sections revealed important properties of the standard beta zeolite (H-BEA-std) used in this work. The properties can be summarized as followed:

1. H-BEA-std is composed of tiny primary crystallites, which can be seen as nano particles (from SEM and FTIR). The BET evaluation confirmed the high external surface area, which is a consequence of this morphology.

2. The three different AlOH species encountered in the IR spectroscopy showed that a deep dealumination has occurred from the simple calcination and transformation into the H\(^+\) form. This aspect is also corroborated from the \(^{27}\)Al MAS NMR results. All kind of aluminum debris is expected to be present in the micropores as well as outside as larger clusters.
Zeolite mordenite shows a restricted transition-state shape selectivity for the alkylation of biphenyl with propylene inferred to the one-dimensional micropore channel structure. Such shape selectivity will not occur on zeolite beta due to the large empty space created at the intersection of the three-dimensional channel structure, which can easily accommodate all dialkylbiphenyl isomers. A product selectivity is then expected as long as the reaction is mass transfer limited. For H-BEA-std a substantial amount of strong Brønsted acid sites are located on the external surface area. Moreover, the accessibility of all active sites within the micropores is also reduced by the presence of aluminum debris, which severely obstruct the micropores. Per contra, the aluminum debris located outside the micropores are likely slightly active but without shape-selective properties (see Figure 14). Thus, the relative rate of the non-shape-selective reaction outside the micropores is amplified to such an extent that makes H-BEA-std just slightly better in terms of selectivity than a common silica-alumina. The acid treatment has then the following advantages:

1. The acid leaching with HCl concentrations lower than 0.1 M mainly extracts the extraframework aluminum permitting a better accessibility of the micropores and a removal of possible non-shape-selective sites. In addition, it would passivate any silica-alumina impurities that could be present from a non-optimal commercial synthesis (see Table 8 and Figure 23).

2. The acid leaching with HCl or HNO₃ solutions with concentrations higher than 1 M removes selectively framework aluminum. In the case of zeolite beta, the aluminum that is preferentially removed is located nearby structural defects and on the external surface area. The NMR results clearly demonstrate this aspect. Thus, the acid treatment with concentrated acid solutions markedly reduces the relative activity of the high external surface area so that the intrinsic shape-selective properties of the beta micropores can come into effect.

The work also demonstrated that the structural integrity of zeolite beta is maintained after the acid treatment. Zeolite beta is resistant to acid attack with HNO₃ concentrations up to 6 M. Some structural rearrangement is observed which somewhat affects the zeolite structure (10-20%). The rearrangement seems to create a new silica amorphous phase that is however complete inactive for the alkylation reaction (see Figure 14).
The small size of the primary beta crystallites would however not be in favor of mass transfer limitations but the experimental data show strong evidences that it is indeed the case:

1. The activity of silica-alumina, which has a lower density of acid sites, is quite higher than the activity of zeolite beta.

2. The increase of the reaction temperature has a beneficial influence on the selectivities to the most slim isomers (4-IPB and 4,4′-DIPB).

3. The activity ratio calculations based on the Thiele modulus and on assuming that the reaction is highly mass transfer limited correspond closely to what is experimentally observed.

Thus the alkylation of biphenyl with propylene is mass transfer limited within the micropores of zeolite beta. It becomes shape-selective because diffusion allows the discrimination between the diffusion rate of the different isomers. The severe mass transfer limitations are caused by configurational diffusion that occurs in the micropores of zeolites. Contrary to bulk or Knudsen diffusion, the diffusion coefficient for configurational diffusion can tremendously vary upon slight change in the geometry of a molecule. This is probably the reason, which accounts to the fact that the alkylation of naphthalene with propylene in zeolite beta is a non-shape-selective process.

2.12. Conclusion

The alkylation of biphenyl and naphthalene with propylene are typical Brønsted acid catalyzed reactions. The activation of propylene proceeds usually well so that moderate to strong Brønsted acid sites are useful to conduct the reaction. We have shown that even γ-alumina is to certain degree active. So the first advantage to submit a zeolite to an acid leaching procedure is to remove or passivate all kind of extra-framework impurities from aluminum clusters to silica-alumina debris. These impurities have shown to be to some extent acidic. However, the most important effect of acid leaching with concentrated acid solutions is to preferentially remove framework aluminum located on the external surface area and on defect sites. Thus, the intrinsic microporous behavior of zeolite beta can come into effect and
a shape-selective mechanism can take place for a reaction that is highly mass transfer limited. In these conditions the alkylation of biphenyl with propylene becomes shape-selective because configurational diffusion allows the discriminated between the diffusion rate of the different isomers. However, this effect does not take place when naphthalene is used as reactant. The shape-selective reaction follows a truly product selectivity and not a restricted transition-state selectivity because the large empty spaces at the intersection of channel in zeolite beta can easily accommodate all isomers. The slight structural rearrangement of zeolite beta after the acid leaching produces an amorphous silica material that is inactive for the reaction.
3. CATALYTIC AND NON-CATALYTIC COUPLING OF p-CHLOROTOLUENE

The purpose of the present work is to develop a new approach for the synthesis of 4,4’-DMB. The potential to turn the Ullmann reaction catalytic will be investigated based on three simple reaction as described in Scheme 12. Simple reaction conditions and mixtures are purposely used to investigate only the effect of the catalytic system on the activity and selectivity. Reaction 1 is the most simple reaction pathway that can undergo p-chlorotoluene (PCT) to form 4,4’-DMB. Chlorine is then the elemental gas produced. Reaction 2 is the non-catalytic reaction comparable to an Ullmann reaction and Reaction 3 is the catalytic alternative with hydrogen as reducing agent.

\[
\begin{align*}
\text{Reaction 1:} & \quad 2 \text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{H}_2\text{C} - \text{CCH}_3 + \text{Cl}_2 \\
\text{Reaction 2:} & \quad 2 \text{Cl} + \text{M}^{(0)} + \text{H}_2 \rightarrow \text{H}_2\text{C} - \text{CCH}_3 + \text{M}^{(x)}\text{Cl}^{(x)} \\
\text{Reaction 3:} & \quad 2 \text{Cl} + \text{H}_2 \rightarrow \text{H}_2\text{C} - \text{CCH}_3 + 2\text{HCl}
\end{align*}
\]

\textbf{Scheme 12: three types of reaction for the synthesis of 4,4’-DMB from PCT}

3.1. The catalytic coupling with chlorine as product

The Deacon reaction [160] is an old procedure for the formation of chlorine from HCl and oxygen. High temperatures are required to liberate the chlorine from the surface of the catalyst (T>400°C). By analogy, one could imagine a similar process where chlorine from PCT is abstracted from the catalyst surface and released as dichlorine at high temperatures. Due to the good stability of the aromatic ring, 4,4’-DMB is a potential product. Thermodynamic calculations are however completely in disagreement with such a mechanism when gaseous chlorine is formed [161]. Thermodynamic equilibrium is nevertheless only valid when the complete reaction is reversible. If a purely radical mechanism plays a critical role, the reaction is likely irreversible producing a mixture of products. For example, a
fraction of 4,4’-DMB formed could further react with gaseous chlorine also produced to form ring-chlorinated 4,4’-DMBs.

Despite these limitations, experiments have been conducted in the gas phase at $T = 500^\circ C$, $P = 1.01$ bar and WHSV = 2.3 h$^{-1}$ over Deacon type catalysts such as Cu(5%)Cl/$\gamma$-Alumina and Cu(5%)spinel/$\gamma$-Alumina as radical generator in order to synthesise 4,4’-DMB. The results obtained show two kinds of characteristic products as analysed from GC-MS. The first group belongs to components of lower molecular weight than PCT with toluene as representative product. The second group, with a quite lower concentration, belongs almost exclusively to components made of two phenyl groups with diphenylmethane as representative element. The reaction mixture obtained has to be regarded with respect to the different C-H and C-Cl bond strengths [162,163]. For a purely radical mechanism, the preferential activation of the C-Cl aromatic bond (96 kcal/mol) over the C-H aromatic bond (110 kcal/mol) is possible due to the lower C-Cl bond strength. However, a more probable intermediate is the benzyl radical from the methyl group present in PCT, which has a bond strength of 85 kcal/mol. The reaction pathway becomes highly complex but can suggest the formation of coupled products such as diphenylmethane.

3.2. The non-catalytic coupling

When reactions are performed with the same conditions as for Reaction 1 ($P = 1$ atm, $N_2 = 80$ mol%, PCT = 20 mol%, catalyst weight = 3 g and WHSV = 2.3 h$^{-1}$) but at lower temperatures, the appearance of 4,4’-DMB is observed on Cu(5%)spinel/$\gamma$-Alumina once Cu is reduced prior to reaction [Figure 30]. The total activity is not high but a closer look is required to understand the nature of the Cu reactivity. The selectivity is very dependent on the reaction temperature. At high temperatures, the formation of toluene is predominant while the selectivity to 4,4’-DMB increases by reducing the temperature. 4,4’-DMB and toluene are the two main products and selectivities to other products like benzene count for less than 10%. The coupling reaction is in competition against the simple dechlorination. Moreover, the results revealed in [Figure 30] are for experimental points, which are taken after 10 min time on stream (TOS). There is a very rapid deactivation of the catalyst due to the oxidation of Cu to Cu (I)Cl.
Figure 30: activity of Cu(5%)spinel/γ-Alumina as a function of temperature in the gas phase for the conversion of PCT \( (TOS = 10 \text{ min}, P = 1.01 \text{ bar}, N_2 = 80 \text{ mol\%}, PCT = 20 \text{ mol\%}, \text{catalyst weight} = 3 \text{ g, WHSV} = 2.3 h^{-1}) \)

Figure 31: the non-catalytic nature of the gas phase reaction with Cu(5%)spinel/γ-Alumina for the conversion of PCT at different temperatures \( (P = 1.01 \text{ bar, } N_2 = 80 \text{ mol\%}, PCT = 20 \text{ mol\%, catalyst weight} = 3 \text{ g, and WHSV} = 2.3 \text{ h}^{-1}) \)
The non-catalytic nature of the reaction is shown in Figure 31 where the yield of 4,4′-DMB is plotted as a function of time on stream for the gas phase reaction at different temperatures. The reaction is completed in less than 30 min at higher temperatures (T > 250°C). At lower temperatures, a physical adsorption phenomenon of 4,4′-DMB seems to have an important effect. The appearance of 4,4′-DMB is likely delayed because 4,4′-DMB is physically adsorbed and desorbed while flowing through the catalyst bed. The normal boiling point of 4,4′-DMB is 295°C and at temperatures as low as 200°C there is obviously an important role of physical forces.

The mechanism of deactivation can be fully understood by comparing the results obtained in the gas phase with the results obtained in the liquid phase (Figure 32). The reaction in the liquid phase is performed like a classical Ullmann reaction with the following conditions: T = 160°C at reflux, Cu-powder weight = 0.15 g, supported metals weight = 3 g, PCT = 10 g and reaction time = overnight (PCT is a solvent for itself since it is used in excess). An experiment with Cu-powder is included for a precise comparison of the activities. The conversions which appear in Figure 32 are based on the total amount of Cu reacted with chlorine as outline in reaction 2. Cu is expected, after reaction, to be present mainly as Cu\(^{1+}\) because of its higher
stability in a non-aqueous environment [164]. As foreseen from the literature [101], the activity of Cu-powder for the coupling of chlorotoluene is totally absent. On the other hand, the conversion over Cu(5%)spinel/γ-Alumina is around 30% with a selectivity higher than 70%.

It is interesting to see the close relation between the gas phase and the liquid phase reactions for Cu(5%)spinel/γ-Alumina. The relative amount of Cu reacted with PCT is 25% for the gas phase reaction at 200°C and 30% for the liquid phase reaction at 160°C. A difference that is less than 20% which indicates a high similarity in the reactivity of PCT with Cu in both phases. The calculation is based on the total amount of Cu on the carrier and not on the amount of Cu which has been reduced during the reduction process. Due to the spinel formation of Cu with alumina, the Cu reduction is likely incomplete [165] and the Cu reactivity is probably underestimated.

The activity and selectivity are also greatly dependent on the nature of the reactive metal used. As indicated in the introduction, Ni particles are also active for the coupling reaction and the use of highly dispersed Ni on γ-alumina may also present some activity. Thus, supported base metals such as Fe, Co and Ni are studied. However, none of them shows better
activity than Cu. In fact, Ni is quite unreactive at low temperatures and the reason of this low reactivity is probably attributed to the formation of very stable Ni aluminate species, which are quite difficult to reduce at low reduction temperatures [166]. Finally, it is worthwhile to note that Pd(5%)/Charcoal yields 4,4’-DMB in negligible amounts.

The type of carrier used and the calcination temperature have also important influences. Cu supported on silica (Aerosil 200) is totally ineffective for the reaction while other carriers such as ZrO₂, TiO₂, Fe₂O₃ and large pore zeolites give only minor activities. Figure 33 shows a typical profile at different calcination temperatures obtained with Cu(5%)/Fe₂O₃. From this figure one can see that the calcination temperature has influences on both the activity and the selectivity. For a Cu(5%)/γ-Alumina, the optimal calcination temperature is around 800°C. At this high temperature Cu has easily reacted with alumina to form a surface spinel [167].

The higher activity associated with Cu(5%)spinel/γ-Alumina is attributed to the higher metal dispersion achieved on γ-alumina. Therefore, TEM images combined with EDX analysis of Cu supported on three different carriers (silica, α-alumina and γ-alumina) have been compared. In all three cases, the preparation conditions are identical and about 20 EDX analysis are performed for each sample after reaction. Figure 34 displays a typical image obtained for each kind of support. The silica material shows Cu particles (CuO or Cu) between 0,1 and 3 µm while the α-alumina material shows a size distribution between 10 and 1000 nm. On both surfaces, Cu is quite heterogeneously distributed and most of the carrier surface is not in intimate contact with the Cu particle. In contrast is Cu(5%)spinel/γ-Alumina where a homogeneous Cu distribution is found. The primary crystal particles of γ-alumina are quite small in the range of 5 to 20 nm, which is common for this type of material. Due to the fine crystal structure, it is not possible to observe distinct Cu particles. The Cu particles are likely to be of the same size as the primary γ-alumina crystallites or are very well intermixed with the alumina. The induced spinel formation prior to reaction preferentially favors this high degree of intermixture. Besides Cu, the element chlorine is also detected which indicates at least some oxidation of Cu with chlorine after reaction.
Figure 34: TEM images of Cu supported on silica (Aerosil 200) (A), α-alumina (EO 19) (B), and γ-alumina (TE 134) (C) (images of the catalysts after reduction)
In the view of the author, the spinel formation with high temperature calcination is an important factor for the high dispersion of Cu particles after reduction. The spinel formation likely tends to spread Cu on the γ-alumina surface. A similar behavior has been recently observed for Ni particles [168]. In this article, the presence of water vapor during the reduction favors the formation of Ni aluminate, which leads to higher Ni dispersion after reduction. In our case, it has not been possible to obtain experimental evidence of this behavior from chemisorption investigation. Reliable size dispersion values for Cu are obtained from chemisorption of N₂O combined with an appropriate experimental apparatus [169]. At this time, such an equipment is not available in our laboratory.

It is logical to conclude that the activity of Cu(5%)spinel/γ-Alumina is mainly based on the high dispersion of reduced Cu which gives access to additional Cu atoms. It is however not the only explanation of the Cu activity on γ-alumina. When an extensive amount of Cu-powder is employed for a common Ullmann reaction, conversion remains absent even when more Cu atoms are accessible [Figure 32]. Hence the reactivity of Cu with PCT is likely a structure sensitive reaction. The reactivity is a function of the Cu crystallite size; the lower the crystallite size, the higher is the coupling reaction.

Finally, the results in the gas phase give useful information concerning the mechanism of an Ullmann reaction and can easily explain the low selectivities usually obtained with that method. The main side reaction, which usually occurs for an Ullmann reaction, is the simple dechlorination. The dechlorination supposes however the involvement of hydrogen in the reaction and the hydrogen can certainly come from the formation of coke precursor and/or polymer fragments on the metallic Cu surface. TPO measurements of the catalysts used in Figure 30 draw a clear image on the involvement of carbon fragments. This is shown in Figure 35 where two characteristic peaks are shown: the first one is related to water physisorbed on the catalyst while the second one refers to the amount of CO₂ detected during the TPO.
Figure 35: TPO measurements of the carbon fragments present on the catalysts used in Figure 30
(oxidation ramp = 5°/min)

The expected behavior is clearly followed. As the temperature of the reaction increases the amount of carbon present on the catalyst increases also. Even at temperatures as low as 200°C, there is still carbon remaining on the surface. Thus, the mechanism involved here is attributed to different atom-atom bond hydrogenolysis [170]. In our case, the role of Cu is to hydrogenolyse selectively the aromatic C-Cl bond toward the C-H bond. The activation energy of C-Cl bond cleavage is hence lower than the activation energy of C-H bond cleavage. As a consequence, the increase of temperature significantly favors the C-H bond cleavage which directly leads to dechlorination by hydrogen transfer and to the formation of toluene and carbon fragments on the metal surface.

3.3. The catalytic coupling with a reducing agent

The main goal of the following investigation is to find out a catalytic alternative to the common Ullmann reaction. The use of a reducing agent is then essential to reactivate the catalyst surface or, in other words, to reduce the free energy of the reaction by producing HCl (reaction 3). The introduction of a reducing agent such as organic acids, alcohols or hydrogen
to capture chlorine as HCl would inevitably favor the simple dechlorination of PCT to toluene. The catalyst system plays then a fundamental role on the selectivity of the reaction.

Before different catalytic systems are investigated, Cu(5%)spinel/γ-Alumina is studied with hydrogen in the same conditions as mentioned above in Figure 30 namely P = 1.01 bar, N₂ = 60 mol%, H₂ = 20 mol%, PCT = 20 mol%, catalyst weight = 3 g and WHSV = 2,3 h⁻¹. Figure 36 shows the conversion of PCT as a function of TOS. The main product is toluene and only traces of 4,4’-DMB are detected. There is a very rapid deactivation of the catalyst with a low residue of activity at higher temperatures (T = 300°C). An important conclusion can be drawn from these results: the oxidation of metallic Cu with PCT is faster then the reduction of CuCl with hydrogen. Thus, Cu alone is not suitable to perform the oxidation/reduction cycle.

The use of Cu in combination with a noble metal is an alternative. Indeed, Cu could play its actual role of oxidation centre where PCT couples to 4,4’-DMB while the noble metal could induce hydrogen chemisorption activity which, in turn, would spillover to the oxidised Cu. Such a mechanism would be comparable to a Mars van Krevelen mechanism [171] performed on a bimetallic catalyst with each metal having its distinct role. Moreover the use of a second
metal with the noble metal is not only limited to Cu. Any metal which can promote oxidation activity is a potential candidate as for example the Pd-Bi combination [172]. The experimental conditions should also be optimised to promote the coupling. That is, PCT concentration should always be kept very high near the active sites to favor the coupling while the concentration of hydrogen should be limited. The use of a three-phase slurry reactor is then appropriate in where the solid phase is the catalyst, the liquid phase PCT and the gas phase hydrogen. In such a reactor, the concentration of PCT is at its maximum and the concentration of hydrogen is a function of its partial pressure and its solubility into PCT.

![Figure 37](image)

**Figure 37:** activity of different noble metals on silica in a three-phase slurry reactor for the conversion of PCT with hydrogen as reducing agent (T=160°C, P H2 = 1.01 bar, catalyst weight = 20 g, and reaction time = 400 min)

The first experiments carried out in these conditions (i.e. T = 160°C, P H2 = 1.01 bar, catalyst weight = 2 g, PCT = 20 g and reaction time = 400 min) show that HCl is easily stripped out of the reaction mixture at a temperature of 160°C. Hence, the need of a base is not essential. The first catalysts studied are noble metals supported on silica (D11-10) in order to evaluate the intrinsic activity of each individual metal. The results obtained with four different noble metals are depicted in [Figure 37](image). Pd is the most active metal. The activity decreases in the order Pd > Pt > Ru > Ag where a metal like Ag is totally ineffective. In all cases, it is not possible to detect any 4,4'-DMB. The actual reaction is indeed very similar to the
dechlorination of aromatic compounds like PCBs, a subject that has recently attracted the attention of many authors for environmental protection reasons [173,174]. The same order of metals reactivity has also been reported [173].

Figure 38: activity of Pd supported on different carriers in a three-phase slurry reactor for the conversion of PCT with hydrogen as reducing agent (catalyst weight = 2 g, PCT = 20 g at 160°C and 30 g at 220°C, and reaction time = 400 min)

The influence of the carrier on the reaction activity and selectivity is shown in Figure 38 for Pd based catalysts. Silica, γ-alumina and carbon with about the same amount of Pd have a similar activity at a temperature of 220°C. In contrast, a catalyst with a higher Pd content has also a higher activity per gram of catalyst. Indeed, Pd(5%)/Charcoal possesses the highest activity even at lower temperatures. The direct use of Pd without any carrier is also active. In this case, Pd is introduced in the reaction mixture as PdCl₂ powder. Pd is in-situ reduced in less than 15 min to black metallic pellets which indicates that the active state of the metal is probably a reduced Pd. The formation of 4,4’-DMB in a significant amount is only possible with a carbon based carrier. All other carriers give marginal traces of 4,4’-DMB. The selectivity of Pd(0.8%)/Carbon is not high (1.5%) but the experimental conditions are not yet optimal. According to our knowledge, there has not been any report in the literature concerning the coupling of chloro-aromatic compounds by such a hydrogenation method in the liquid phase.
The use of a more easily oxidised metal such as Cu in combination with a noble metal is the main objective of this work. Therefore, a large number of bimetallic catalysts are screened. The catalysts are mainly composed of Pd combined with metals such as Ti, Fe, Ni, Cu, Ag, Hg and Bi and supported on different carriers. Figure 39 shows only the relevant results of the catalysts screening. Firstly, Pd(5%)/Charcoal, which is inactive for the coupling of PCT becomes active when combined with Bi. Secondly, the introduction of an additional metal to Pd always decreases the catalytic activity. Pd(0.8%)/Carbon remains the most active catalyst when compared to its bimetallic variants. This is consistent with the results obtained by Ohnishi et al. in terms of activity [175]. Thirdly, on carbon based catalysts, the increase of selectivity for the formation of 4,4’-DMB is only observed for a bimetallic combination of Pd and Hg. Thus, the appearance of 4,4’-DMB for a Pd-Bi combination and the increase of selectivity for a Pd-Hg combination confirm the bimetallic usefulness.

![Figure 39: activity of bimetallic metals supported on carbon in a three-phase slurry reactor for the conversion of PCT with hydrogen as reducing agent (T = 220°C, $P_{H2} = 0.85$ bar, catalyst weight = 2 g, PCT = 30 g, and reaction time = 400 min)](chart)

The hydrogen partial pressure has to be reduced in order to render the experimental conditions optimal for the formation of 4,4’-DMB. Figure 40 and Figure 41 show that, at two different temperatures, the selectivity is increased on Pd(0.8%)+Ti(3%)/Carbon or Pd(0.8%)/Carbon...
with a reduction in the hydrogen partial pressure. This effect is however not observed on a Pd(5%)/Charcoal. On this catalyst, it is not possible to form 4,4’-DMB in any significant amount with a lower hydrogen pressure. Thus, the formation of 4,4’-DMB is more or less an intrinsic behavior of the carbon carrier.

The total activity decreases significantly when the hydrogen partial pressure is reduced. The coupling reaction is however not as much affected as the dechlorination. It is nonetheless important to recall that the formation of 4,4’-DMB is definitively catalytic even at very low conversion. Figure 32 shows that 4,4’-DMB is not produced on a Pd(0.8%)/Carbon when hydrogen is not present. Moreover, the turnover number (mol of 4,4’-DMB formed / No. of Pd atoms) for this catalyst during the reaction is around 4 at a low conversion of 7%. Toluene and 4,4’-DMB are two stable products, which do not undergo consecutive serial reactions under these conditions as, for example, to the ring hydrogenated products (methylcyclohexane and 4,4’-dimethyl-1,1’bicyclohexyl). Thus, the total yield to 4,4’-DMB at a low hydrogen partial pressure can be increased by a longer reaction time.

Figure 40: influence of the hydrogen partial pressure on the conversion of PCT in a three-phase slurry reactor on Pd(0.8%)+Ti(3%)/Carbon (T = 220°C, catalyst weight = 2 g, PCT = 30 g, and reaction time = 400 min)
Figure 41: influence of the hydrogen partial pressure on the conversion of PCT in a three-phase slurry reactor on Pd(5%) and Pd(0.8%)/Carbon (T = 160°C, catalyst weight = 2 g, PCT = 20 g, and reaction time = 400 min)

Finally, the last important factor, which can influence the selectivity, is the temperature. The influence of the temperature on the conversion and on the selectivity to 4,4’-DMB is shown in Figure 42. From this figure, it is seen that the conversion increases with the elevation of the temperature while the selectivity to 4,4’-DMB remains stable and very low. There is likewise one situation where the temperature might not at all change the selectivity of the reaction. It is when both reactions, namely the dechlorination and the coupling, have a similar activation energy. This situation is possible if both reactions have the same rate-limiting step. The activation of PCT to form a chemisorbed chlorine and a tolyl group on the metal surface is a probable rate-limiting step for both reactions. Moreover, if both reactions have a similar activation energy, the corresponding value lies around 50 kJ/mol. This value is not high and the reaction may be limited by internal diffusion [8], but when it is compared to the literature dealing with dechlorination, a similar value is also obtained [174]. Hence, the reaction is most likely kinetically controlled with a rate-limiting step based on the activation of PCT.
3.4. Is the catalytic reaction structure sensitive?

One of the first parameters that should be investigated with supported metal catalysts is whether or not the reaction is structure sensitive [170]. In other words, is the reaction selectivity influenced by the dispersion of the metal? This could be the reason why Pd(0.8%)/Carbon is the most effective catalyst. In order to evaluate this parameter, four Pd/Carbon catalysts are prepared with various Pd contents and dispersions. They are characterized with CO chemisorption and the results are presented in Table 12.

From that table, it is well demonstrated that when the Pd content of the four prepared catalysts is increased, the dispersion is consequently reduced from 40 to 8%. The main effect of increasing the amount of Pd is an enlargement of the metal particles. This is obvious for a Pd concentration between 1 and 4% where there is no net increase in the amount of CO adsorbed on the catalyst. For a concentration of Pd lower than 1% there is an increase in the CO uptake which is however not linear with the increase of Pd content. Such a behavior has been reported in the literature [176] where the high dispersion obtained for low concentration of metals is attributed to the strong adsorption forces between the soluble metal precursor and
the high surface area of the carrier during the impregnation. At higher metal concentration (metal > 1%), the adsorption sites are rapidly saturated and the excess of metal contributes only in the formation of larger particles during the catalyst activation. In contrast is the commercial material (Pd(0.8%)/Carbon), which shows a very low CO volume uptake and consequently a low dispersion.

Table 12: some physical and reaction properties of the Pd supported carbon catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>V. adsorbed (cm³/g STP)</th>
<th>Dispersion (%)</th>
<th>Initial activity (mol/s)</th>
<th>TOF (mol/site/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(0.8%)/Carbon (from J.M.)</td>
<td>0.06</td>
<td>6</td>
<td>1.6×10⁻⁷</td>
<td>0.019</td>
</tr>
<tr>
<td>Pd(0.5%)/Carbon</td>
<td>0.25</td>
<td>40</td>
<td>3.0×10⁻⁷</td>
<td>0.008</td>
</tr>
<tr>
<td>Pd(1%)/Carbon</td>
<td>0.42</td>
<td>33</td>
<td>3.9×10⁻⁷</td>
<td>0.006</td>
</tr>
<tr>
<td>Pd(2%)/Carbon</td>
<td>0.44</td>
<td>18</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pd(4%)/Carbon</td>
<td>0.40</td>
<td>8</td>
<td>3.4×10⁻⁷</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Figure 43: comparison of the carbon based catalysts with different Pd dispersions for the coupling of PCT in the liquid phase (T = 160°C, Pₓ₂ = 0.20 bar, PCT = 20 g, and catalyst weight = 2 g)

The activity and selectivity of these catalysts are shown in Figure 43. The activity is maintained low in order to compare the selectivity at a low conversion (differential modus). The four prepared catalysts are compared under an identical conversion and their...
corresponding selectivity to the formation of 4,4’-DMB is very low. It is not possible to observe a major change in selectivity with the metallic dispersion. Hence, the reaction can be considered as structure insensitive in terms of selectivity.

![Figure 44: kinetic behavior of the Pd supported on carbon catalysts studied in Figure 43](image)

The kinetic behavior of the reaction is depicted in Figure 44. The curves have been obtained from the titration of the HCl produced and they represent the total conversion of PCT. Due to some startup effect, the initial catalytic activity is obtained from the slope of the curve between 5 and 20 h (Table 12). The most relevant result of Table 12 is nonetheless the turnover frequency (TOF) which represent the number of mole of PCT converted divided by the number of surface Pd atom per second. The same TOF is observed (within the experimental errors) for the three prepared catalysts. Thus, the reaction is also structure insensitive in terms of activity. In the newly published book from Somorjai [170], many kinetic parameters are given for reactions catalyzed by metals. It is interesting to notice that the specific reaction rate obtained in this work are located in the lower activity region usually encountered for hydrogenation reactions (0.01-5 mol/site/s). The result is not surprising because in our case the reaction temperature and the hydrogen partial pressure are relatively low.

The difference in specific activity between Pd(0.8%)/Carbon and the other prepared carbon catalysts is important. Pd(0.8%)/Carbon has a three fold higher specific activity. This might
be the reason why a better selectivity is obtained over this catalyst. The explanation probably involves a metal support interaction (MSI) between the Pd particles and the carbon from the high surface area carrier. Indeed Krishnankutty et al. [177-179] have recently reported the suppression of hydrogen chemisorption and hydride formation in Pd crystallites dispersed on high surface area turbostratic carbon black supports. The reason of this phenomenon was the incorporation of carbon in the Pd lattice. In our case, Pd(0.8%)/Carbon is also a high surface area turbostratic carbon black that likely behaves in the same manner. However, Pd might remain active for the chemisorption of chlorine during the reaction and the real catalyst activity being underestimated. The expansion of the Pd lattice by incorporating carbon and the consequent reduction in \( \beta \)-hydride formation is probably the reason for this gain in selectivity. Less hydrogen is then present close to the active sites.

3.5. Conclusion

The formation of 4,4'-dimethylbiphenyl (4,4'DMB) using p-chlorotoluene (PCT) is not possible by a radical mechanism at high temperatures. The main reactions are the dechlorination of PCT and the coupling to diphenylmethane like molecules. The lower bond strength of the methyl group present in PCT can explain the appearance of the second product.

The Ullmann type of reaction with Cu and PCT to form the linear molecule 4,4'-DMB is possible when Cu is activated on a carrier. \( \gamma \)-Alumina is the most appropriate material especially when calcined with the metal at 800°C to form a surface spinel. The surface spinel induces a high metal dispersion after reduction. The loss of selectivity at higher temperatures is caused by the formation of carbonaceous residue on the metal which leads to rapid hydrogen transfer and simple PCT dechlorination. Moreover, the formation of carbonaceous material when no hydrogen is present in the feed starts at temperatures as low as 200°C.

A catalytic alternative with hydrogen of the aforementioned reaction is the use of Pd supported on carbon. It is believed that C-C coupling of chloro-aromatic compounds is for the first time reported under typical hydrogenation conditions. The catalytic system plays a major role on the selectivity. Pd-Hg/Carbon and Pd-Bi/Charcoal combinations have shown to slightly increase the selectivity. Yet, the bimetallic screening is only partial and other
bimetallic systems might prove quite more efficient. The catalytic reaction is structure insensitive and the poisoning effect of Pd from carbon of the carrier is a probable explanation for an increase of selectivity by reducing the concentration of hydrogen on the active sites.
D. GENERAL CONCLUSION

The aim of this work was to find out new chemical routes for the synthesis of dialkylaromatic compounds based on heterogeneous catalysis. The first molecule of interest was p-cymene and its synthesis was studied from the dehydrogenation of naturally occurring terpenes such as α-pinene. The second group of molecules that were investigated in this work concerned binuclear aromatic compounds. 4,4’-diisopropylbiphenyl (4,4’-DIPB) and 2,6-diisopropyl-naphthalene (2,6-DIPN) were produced from the isopropylation of biphenyl or naphthalene using an acid treated zeolite beta as shape-selective catalyst. In contrast, the less bulky 4,4’-dimethylbiphenyl was synthesized according to a new kind of catalytic Ullmann coupling starting from p-chlorotoluene (PCT), which already possess the regioselective information.

The dehydrogenation of α-pinene to p-cymene over carriers impregnated with Pd showed that an optimal acidic strength was required to cleave selectively the C-C bond in the cyclobutane ring of α-pinene. Too strong acid sites such as in zeolites favored side reactions like oligomerization and cracking. Too weak acid sites failed to cleave the aforementioned C-C bond and rapid hydrogenation of the α-pinene was a consequence. Hydrogenolysis was also a major side reaction leading to tetramethylcyclohexanes. A reaction mechanism was proposed in which first isomerization is involved followed by hydrogenation/dehydrogenation to stabilize the components. The catalyst has a dual functionality with the acid sites in charge of isomerization and the metallic sites responsible of hydrogenation/dehydrogenation. The use of crude sulfate turpentine (CST) as raw material showed that α-pinene has a similar reactivity as β-pinene and high yields of p-cymene could be obtained from this cheap starting material. The sulfur remained however a major drawback causing catalyst poisoning.

The results concerning the alkylation with propylene demonstrated that zeolite beta is intrinsically a shape-selective catalyst with biphenyl as reactant. This phenomena is however not observed when naphthalene is used as reactant. Although, the primary crystallites of zeolite beta were very tiny, the reaction with biphenyl was mass transfer limited attributed to configurational diffusion of the bulky products. Three experimental evidences supported this view namely (i) the general lower activity of zeolite beta in comparison to silica-alumina, (ii) the effect of temperature which favored the most slim isomers at higher temperatures, and (iii)
the non-linear relation between the decrease in the number of Brønsted acid sites and the loss of catalytic activity. Zeolite beta without alteration demonstrated poor shape-selective properties and modification by acid leaching with a concentrated solution was required to observe shape selectivity. The acid leaching had for effect to remove selectively framework aluminum atoms from position close to defect sites and on the external surface area. The consequences were a passivation of this very large surface area so that the intrinsic properties of the micropores could come into effect.

The formation of 4,4’-DMB was studied from the conversion of PCT over three types of reactions. The first type of reaction investigated was the coupling of two PCT molecules by producing chlorine. The reaction is thermodynamically unfavorable and 4,4’-DMB was not detected. The second type of reaction was comparable to a classical Ullmann reaction. It was shown that Cu supported on γ-alumina is more reactive for the coupling than Cu-powder alone. The third type of reaction was actually the purpose of section 3 and concerned a catalytic alternative of the Ullmann reaction with hydrogen as reducing agent. The formation of 4,4’-DMB was feasible though in very low yield. The activity and selectivity were dependent on the type of metal and carrier used and also on the hydrogen partial pressure. The best catalyst was a Pd supported on carbon and bimetallic mixtures such as Pd-Hg and Pd-Bi showed also some benefits. To our knowledge, it is the first time that the formation of 4,4’-DMB over typical hydrogenation/dechlorination conditions is reported.

In conclusion, the work investigated three possible chemical routes for the synthesis of linear dialkylaromatic compounds; each method with its advantages and drawbacks. The route based on chloro chemistry has no real industrial potential due to the very low yield. The alkylation with zeolite beta has not reached the selectivity level encountered with zeolite mordenite and is therefore not worth to be studied further. The production of p-cymene from naturally occurring products can remain an attractive alternative if the yield is further increased up to 80%. One avenue to investigate is the use of a bimetallic catalyst. For example the addition of Cu to Pd would likely reduce the hydrogenolysis function of the catalyst and promote the formation of p-cymene at higher temperatures. Additional experiments are for sure worth to try.
E. EXPERIMENTAL PROCEDURE

1. CATALYSTS PREPARATION

The catalysts were mainly zeolites and metals supported on high surface area carriers. Table 13 and Table 14 make an inventory of all the catalysts studied in this work with their respective label, laboratory code and corresponding characteristics. The starting zeolites as well as the oxide carriers were commercial materials obtained from catalyst manufacturers. There are four final commercial catalysts namely Pd(0.8%)/Carbon and Pd(5%)/Charcoal from Johnson Matthey, Pd(5%)+Bi(5%)/Charcoal from Degussa, and Pd(5%)/CaCO₃ from Engelhard. Lastly, Cu-powder (Cu for the organic synthesis) and pure PdCl₂ were purchased from Aldrich.

Table 13: list of the zeolites used in this work

<table>
<thead>
<tr>
<th>No.</th>
<th>Label used in this work</th>
<th>Laboratory code</th>
<th>SiO₂/Al₂O₃</th>
<th>Precursor or commercial sample</th>
<th>BET area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silicalite</td>
<td>HB 97/135</td>
<td>&gt; 2000</td>
<td>Synthesized according to reference [175]</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>Na-ZSM-5</td>
<td>HBV 97/16</td>
<td>75</td>
<td>PQ CBV 8020</td>
<td>430</td>
</tr>
<tr>
<td>3</td>
<td>H-ZSM-5</td>
<td>---</td>
<td>ca. 75</td>
<td>Na-ZSM-5, ion exchanged twice, calcined</td>
<td>ca. 430</td>
</tr>
<tr>
<td>4</td>
<td>NH₄₃-MOR-std</td>
<td>HV 95/40</td>
<td>22</td>
<td>PQ CBV 20A</td>
<td>ca. 456</td>
</tr>
<tr>
<td>5</td>
<td>H-MOR-std</td>
<td>HV 95/40 s.c.</td>
<td>22</td>
<td>NH₄₃-MOR, calcined</td>
<td>456</td>
</tr>
<tr>
<td>6</td>
<td>H-MOR-HCl</td>
<td>HB 99/65</td>
<td>80</td>
<td>H-MOR-std, leached (1 M HCl, 16 h), calcined</td>
<td>464</td>
</tr>
<tr>
<td>7</td>
<td>H-MOR-HNO₃</td>
<td>HB 99/67</td>
<td>240</td>
<td>H-MOR-HCl, leached (6 M HNO₃, 16 h), calcined</td>
<td>450</td>
</tr>
<tr>
<td>8</td>
<td>H-MOR-2HNO₃</td>
<td>HB 99/75</td>
<td>400</td>
<td>H-MOR-HNO₃, leached (6 M HNO₃, 16 h), calcined</td>
<td>445</td>
</tr>
<tr>
<td>9</td>
<td>TEA-BEA-std</td>
<td>HV 93/23</td>
<td>---</td>
<td>PQ Valfor CP-806 B25</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>Na-BEA-std</td>
<td>HV 93/23 s.c.</td>
<td>28</td>
<td>TEA-BEA-std, calcined</td>
<td>---</td>
</tr>
<tr>
<td>11</td>
<td>NH₄₃-BEA-std</td>
<td>HB 99/21</td>
<td>28</td>
<td>Na-BEA-std, ion exchanged twice</td>
<td>ca. 578</td>
</tr>
<tr>
<td>12</td>
<td>H-BEA-std</td>
<td>HB 99/21 s.c.</td>
<td>28</td>
<td>NH₄₃-BEA-std, calcined</td>
<td>578</td>
</tr>
<tr>
<td>13</td>
<td>H-BEA-HCl</td>
<td>HB 99/64</td>
<td>202</td>
<td>H-BEA-std, leached (1 M HCl, 16 h), calcined</td>
<td>546</td>
</tr>
<tr>
<td>14</td>
<td>H-BEA-HNO₃</td>
<td>HB 99/66</td>
<td>1100</td>
<td>H-BEA-HCl, leached (6 M HNO₃, 16 h), calcined</td>
<td>539</td>
</tr>
<tr>
<td>15</td>
<td>H-BEA-2HNO₃</td>
<td>HB 99/81</td>
<td>1200</td>
<td>H-BEA-HNO₃, leached (6 M HNO₃, 16 h), calcined</td>
<td>541</td>
</tr>
</tbody>
</table>

The starting zeolites were commercially available with the exception of silicalite which was synthesized according to the classical route, as described in reference [180]. The zeolites in the sodium form were transformed into the NH₄⁺ form by ion exchange twice with NH₄NO₃ (1 h, 90°C) and then thoroughly washed. The H⁺ form was obtained by a standard
calcination procedure at 540°C (6 h) with a temperature ramp of 2°/min preceding a drying at 120°C (1.5 h). This procedure was also used to activate the catalyst before the acid catalyzed reactions to remove physisorbed water. The beta and mordenite standard zeolites were modified according to acid leaching procedures in three steps. The first step was with a 1 M HCl solution, the second step with a 6 M HNO₃ solution and the third step again with a 6 M HNO₃ solution (all overnight, 16 h). It is important to note that between each step a standard calcination procedure was performed.

Table 14: list of the supported metal catalysts used in this work

<table>
<thead>
<tr>
<th>No.</th>
<th>Label used in this work</th>
<th>Laboratory code</th>
<th>Metal (%)</th>
<th>Carrier origin</th>
<th>BET area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/Aerosil</td>
<td>HB 97/90</td>
<td>0.5</td>
<td>Silica, aerosil 200, Degussa</td>
<td>190</td>
</tr>
<tr>
<td>2</td>
<td>Pd/Silicalite</td>
<td>HB 97/135</td>
<td>0.5</td>
<td>Zeolite</td>
<td>360</td>
</tr>
<tr>
<td>3</td>
<td>Pd/H-ZSM-5</td>
<td>HB 99/78</td>
<td>0.5</td>
<td>Zeolite</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>Pd/H-MOR</td>
<td>HB 99/77</td>
<td>0.5</td>
<td>Zeolite</td>
<td>550</td>
</tr>
<tr>
<td>5</td>
<td>Pd/D-10-10</td>
<td>HB 99/76</td>
<td>0.5</td>
<td>γ-Alumina, D-10-10, BASF</td>
<td>190</td>
</tr>
<tr>
<td>6</td>
<td>Pd/D-11-10</td>
<td>HB 99/80</td>
<td>0.5</td>
<td>Silica, D-11-10, BASF</td>
<td>170</td>
</tr>
<tr>
<td>7</td>
<td>Pd-Na/D-11-10</td>
<td>HB 96/171</td>
<td>0.5; 1</td>
<td>Silica, D-11-10, BASF</td>
<td>175</td>
</tr>
<tr>
<td>8</td>
<td>Cu(5%)spinel/γ-Alumina</td>
<td>HWE 0076 A</td>
<td>5</td>
<td>γ-Alumina, TE 134, CONDEA</td>
<td>152</td>
</tr>
<tr>
<td>9</td>
<td>Cu(5%)/α-Alumina</td>
<td>---</td>
<td>5</td>
<td>α-Alumina, EO 19, Ceramtec</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Cu(5%)/Silica</td>
<td>HWE 0082</td>
<td>5</td>
<td>Silica, aerosil 200, Degussa</td>
<td>145</td>
</tr>
<tr>
<td>11</td>
<td>Cu(5%)/Fe₂O₃</td>
<td>---</td>
<td>5</td>
<td>Fe₂O₃</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>Pd(1%)/Silica</td>
<td>HWE 0185</td>
<td>1</td>
<td>Silica, D-11-10, BASF</td>
<td>ca. 190</td>
</tr>
<tr>
<td>13</td>
<td>Pt(1%)/Silica</td>
<td>HWE 0189</td>
<td>1</td>
<td>Silica, D-11-10, BASF</td>
<td>ca. 190</td>
</tr>
<tr>
<td>14</td>
<td>Ru(1%)/Silica</td>
<td>HWE 0191</td>
<td>1</td>
<td>Silica, D-11-10, BASF</td>
<td>ca. 190</td>
</tr>
<tr>
<td>15</td>
<td>Ag(1%)/Silica</td>
<td>HWE 0187</td>
<td>1</td>
<td>Silica, D-11-10, BASF</td>
<td>ca. 190</td>
</tr>
<tr>
<td>16</td>
<td>Pd(1%)/Alumina</td>
<td>---</td>
<td>1</td>
<td>α-Alumina, TE 134, CONDEA</td>
<td>ca. 152</td>
</tr>
<tr>
<td>17</td>
<td>Pd(5%)/CaCO₃</td>
<td>HV 00/18</td>
<td>5</td>
<td>CaCO₃, M 776/EL, Engelhard</td>
<td>9</td>
</tr>
<tr>
<td>18</td>
<td>Pd(5%)/Charcoal</td>
<td>HWE 0032</td>
<td>5</td>
<td>Charcoal, Type 38H, Johnson Matthey</td>
<td>796</td>
</tr>
<tr>
<td>19</td>
<td>Pd(5%)+Bi(5%)/Charcoal</td>
<td>---</td>
<td>5; 5</td>
<td>Charcoal, CE 196 XRA/W, Degussa</td>
<td>734</td>
</tr>
<tr>
<td>20</td>
<td>Pd or Pd(0.8%)/Carbon</td>
<td>HWE 0033</td>
<td>0.8</td>
<td>Carbon type 86, Johnson Matthey</td>
<td>1365</td>
</tr>
<tr>
<td>21</td>
<td>Pd(0.1%)/Carbon</td>
<td>HB 99/43</td>
<td>0.1</td>
<td>Carbon, 1.02518, Merck (HV 00/17)</td>
<td>ca. 1366</td>
</tr>
<tr>
<td>22</td>
<td>Pd(0.5%)/Carbon</td>
<td>HB 99/44</td>
<td>0.5</td>
<td>Carbon, 1.02518, Merck (HV 00/17)</td>
<td>ca. 1366</td>
</tr>
<tr>
<td>23</td>
<td>Pd(1%)/Carbon</td>
<td>HB 99/45</td>
<td>1</td>
<td>Carbon, 1.02518, Merck (HV 00/17)</td>
<td>ca. 1366</td>
</tr>
<tr>
<td>24</td>
<td>Pd(2%)/Carbon</td>
<td>HB 99/46</td>
<td>2</td>
<td>Carbon, 1.02518, Merck (HV 00/17)</td>
<td>ca. 1366</td>
</tr>
<tr>
<td>25</td>
<td>Pd(4%)/Carbon</td>
<td>HB 99/47</td>
<td>4</td>
<td>Carbon, 1.02518, Merck (HV 00/17)</td>
<td>ca. 1366</td>
</tr>
<tr>
<td>26</td>
<td>Pd(0.8%)+Cu(3%)/Carbon</td>
<td>HB 98/52</td>
<td>0.8; 3</td>
<td>Carbon, Type 38H, Johnson Matthey</td>
<td>ca. 1365</td>
</tr>
<tr>
<td>27</td>
<td>Pd(0.8%)+Ag(3%)/Carbon</td>
<td>HB 98/54</td>
<td>0.8; 3</td>
<td>Carbon, Type 38H, Johnson Matthey</td>
<td>ca. 1365</td>
</tr>
<tr>
<td>28</td>
<td>Pd(0.8%)+Ti(3%)/Carbon</td>
<td>HB 98/71 or 64</td>
<td>0.8; 3</td>
<td>Carbon, Type 38H, Johnson Matthey</td>
<td>ca. 1365</td>
</tr>
<tr>
<td>29</td>
<td>Pd(0.8%)+Bi(3%)/Carbon</td>
<td>HB 98/65</td>
<td>0.8; 3</td>
<td>Carbon, Type 38H, Johnson Matthey</td>
<td>ca. 1365</td>
</tr>
<tr>
<td>30</td>
<td>Pd(0.8%)+Hg(3%)/Carbon</td>
<td>HB 98/56</td>
<td>0.8; 3</td>
<td>Carbon, Type 38H, Johnson Matthey</td>
<td>ca. 1365</td>
</tr>
</tbody>
</table>

The commercial carriers were impregnated with metals to create mono and bimetallic catalysts (Table 14). The general wet impregnation procedure was as followed for Cu(5%)/γ-Alumina: 15.7 g of Cu acetate were dissolved in 200 ml of distilled water and were added to
100 g extrudates of γ-alumina. This mixture was stirred in a flask for a few hours and the water subsequently removed under vacuum using a rotavapor. The catalyst was then dried overnight at 120°C and calcined at the appropriate temperature. It is noted that a Cu(5%)/γ-Alumina, which was calcined at 800°C is called in this paper: Cu(5%)spinel/γ-Alumina. A similar method was also used to prepare the other mono or bimetallic catalysts from the starting commercial carriers but with the following salts: Pd(NH₄)(NO₃)₂ for Pd, Pt(NH₄)₄Cl₂ for Pt, RuCl₃ for Ru, AgNO₃ for Ag, TiCl₃ in HCl for Ti, Bi(NO₃)₃ for Bi, HgCl₂ for Hg, NaOH for sodium, and in one case CuCl₂ for Cu. The majority of the catalysts were calcined (standard oven) and reduced under hydrogen flow (2 l/h, 300°C, and 3 h). It is to note that the Pd based catalysts were not calcined but in-situ reduced during the startup period with a heating rate of 5%/min to the reaction temperature. Cu(5%)Cl/γ-Alumina and Pd(0.8%)+Hg(3%)/Carbon were only dried.

2. REACTION CONDITIONS

The reactions with terpenes were performed in the gas phase, the alkylation reactions in the liquid phases and the Ullmann type of coupling reactions in both phases. For the gas phase reactions, the catalysts were formed into pellets, crushed and sieved to granules of 1.0-1.6 mm. The granules were packed into a 6 mm stainless steel tubular reactor in the form of a coil. The reactor was located at the center of a conventional tube such that isothermal conditions were obtained in the catalyst bed. The reactants α-pinene (Firmenich), camphene (Fluka), pinane (Fluka), crude sulfate turpentine (Kraft paper mill, La Tuque, Canada), and p-chlorotoluene (Fluka) were fed into the reactor using hydrogen or nitrogen as carrier gas under atmospheric pressure. The products were condensed at 2°C at the reactor outlet. Detailed experimental conditions were depicted on each figure.

For the liquid phase reactions with PCT, two types of reactors were used, namely a common laboratory flask and an autoclave. The flask is used to perform the typical Ullmann reactions where PCT was heated at reflux (160°C) and the carrier was introduced with the externally reduced metal. Care had to be taken in order to introduce the reduced metal in an inert environment. The autoclave was used as a three-phase slurry reactor. The reactor was operated in a semi-continuous way where the stationary phase was the catalyst and PCT and the continuous phase a mixture of hydrogen and nitrogen bubbling at a rate of 75 ml/min
(normal conditions). A pressurized condenser was attached to the reactor in order to return immediately the liquid, which had evaporated with the bubbling gas. The autoclave permitted liquid reactions with PCT at higher temperatures by maintaining a higher pressure of nitrogen and hydrogen (P_{\text{total}} = 7 \text{ bar}). Consequently, the concentration of hydrogen in the liquid phase was controlled by its partial pressure (details on each figure).

The alkylation reactions were also performed in the liquid phase using a similar autoclave as previously described. Instead of having a gas bubbling though the liquid, the reacting gas (propylene) was fed by maintaining a constant pressure of 10 bar over the reacting liquid. The reaction mixture is then well agitated to avoid any gas-liquid mass transfer limitations. The exact feed composition is depicted on each figure.

In some cases the carrier acidity was investigated with test reactions. Isopropanol dehydration was used for the catalysts with moderate and weak acid sites, using the same conditions as for the dehydrogenation, excepted that nitrogen was used as carrier gas. Biphenyl isopropylation was used for the catalysts with strong and moderate acid sites as just described.

3. CHROMATOGRAPHY AND MASS SPECTROSCOPY

All products and reactants were analyzed with gas chromatography on a HP 6890 GC Chemstation supplied with a flame ionization detector (FID). For terpenic products, the apparatus was equipped with a 60 m OV-1701-CB column operated isothermally at 80°C to maximize the product separation followed by a temperature increase to 240°C for complete desorption of products. The products were all similar (C_{10}) so that the mass factor responses were assumed to be 1. The category of the product (bicyclic, monocyclic, aromatic etc.) was ascertained with GC-MS (Varian Saturn 3) and some products identification was established by comparison of retention time with known substances (if available).

For PCT derivatives, the GC apparatus was equipped with a 30 m HP5 column operated between 50 and 270°C with a ramp of 10°/min. The two main products were 4,4’-DMB and toluene and they could be purchased (Aldrich and Fluka respectively), so that a standard area normalization method was applied for the quantitative analysis (PCT = 1, 4,4’-DMB = 0.72, and toluene = 0.75). The conversion was evaluated from the percentage of transformed PCT.
The selectivity was defined as the percentage of the consumed reactant that formed the desired product. For example, 4,4’-DMB had two moles of PCT in its structure in comparison to toluene which had only one.

For biphenyl derivatives, the GC apparatus was equipped with a 30 m HP5 column operated between 50 and 270 with a ramp of 10°/min. For naphthalene derivatives, the GC apparatus was operated first at 100°C for 3 min than steadily increased to 270°C at a rate of 8°/min. The GC peak assessment was straightforward because it was possible to buy all the desired isomers namely 4-IPB (Aldrich), 4,4-DIPB (Avocado), 2-IPN (Avocado), 2,6-DIPN (Sigma-Aldrich Rare Chemical), and 2,7-DIPN (Frinton Laboratories). The remaining compounds were characterized by their molecular weight in the GC-MS. Moreover it was possible to show experimentally that the purchased isomers had all the same mass factor response. It was then assumed that all the products had similar mass factor responses. It is important to remember that the selectivity of one component referred to its relative concentration with the other isomers in the same product distribution, for example, 4,4’-DIPB in relation with the 16 other twice alkylation.

4. CHARACTERIZATION BY BET, ICP, TG, XRD, SEM, AND TEM

The catalysts were characterized with nitrogen sorption at –196°C (Micromeretics ASAP 2010) using the Brunauer-Emmet-Teller method to determine the BET surface area [181]. The micro and mesopore volumes as well as the external surface area were determined by the Barret-Joyner-Halenda (BJH) and the t-plot methods [181,182].

The catalysts were also characterized with induced couple plasma coupled with atomic emission spectroscopy (ICP AES) (Spectroflame D, Spectro Analytic Instrument). The typical procedure was to dissolve 30 mg of catalyst in a 5 ml 40% HF solution and dilute it afterwards with 45 ml of distilled water.

The amount of coke was evaluated by thermogravimetric analysis (TG) (Netsch 209/2/E equipped with a STA 409 controller) with a heating rate of 5°/min under flowing air using alumina-crucibles and α-alumina as reference material.
The zeolite crystallinity was ascertained from x-ray diffraction measurements (XRD) (Siemens Diffraktometer D 5000, CuKα-emissions, secondary monochromator, variable diaphragm V2O, Ni-filter, and a rotation speed of 1.2°/min). Before each measurement the samples were crushed to a fine powder. The integrated intensity of the signal at $\theta = 22.4°$ was used for the evaluation the crystallinity for the beta zeolites while the signals at $\theta = 9.7, 13.5, 17.7, 22.5, 25.8,$ and $26.5°$ were used for the mordenite zeolites.

The transmission electron microscope (TEM) images combined with energy dispersive x-ray (EDX) analysis of the catalysts after reaction were obtained from the analytical department of Hoechst AG (Philips CM30 and EDAX PV9900). The scanning electron microscope (SEM) images of the zeolites were obtained from the “Gemeinschaftslabor für Elektronenmikroskopie” of the RWTH-Aachen without further information.

5. CHARACTERIZATION BY TPD, TPO AND CO CHEMISORPTION

The catalyst acidity was in some cases determined by temperature programmed desorption of ammonia (TPD). The catalyst was saturated with ammonia at 100°C, followed by an evacuation in helium of exactly 3 h after which the measurements were carried out with a ramp of 10°/min up to 800°C. The ammonia evolved was detected by titration. Temperature programmed oxidation (TPO, ramp = 5°/min) carried out on some catalysts were obtained from the analytical department of Hoechst AG without further information.

CO chemisorption isotherms were also determined on the Micromeretics ASAP 2010 also used for the BET. The catalyst was pre-treated in the same manner as it was activated before reaction. After flushing with helium for 30 min and evacuation at 300 and 25°C ($1\times10^{-4}$ mbar, 30 min), the measurements were performed at 25°C between 0.25 and 30 mbar according to the dual isotherms technique developed by Yates and Sinfelt [183]. The isotherm was fitted with a Langmuir model of non-dissociate CO adsorption to evaluate the volume required to form a monolayer. With this dual method it was possible to evaluate only the irreversible CO chemisorption with the weakly bonded CO eliminated from the isotherm. A stoichiometry of 0.6 (CO/M) was assumed to calculate the metallic dispersion [184] while the metallic crystallite diameter was evaluated from the expression disclosed in reference [185].
6. CHARACTERIZATION BY FTIR

Fourier transformed infrared (FTIR) spectroscopy was carried out with a Nicolet Protégé 460 device. In a typical experiment, 10 mg of the zeolite were pressed into a self-supported wafer of 13 mm in diameter. The wafer was fixed by stainless steel holders and introduced into a vacuum cell. The cell was placed in the IR-apparatus and heated up to 450°C for 6 h under a flow of air with the same procedure as the standard calcination. Vacuum was afterwards brought into the cell (2×10⁻² mbar) and the temperature was cooled down to 150°C. The measurements were taken at this final temperature in the range of 1000-4000 cm⁻¹. The intensities of the hydroxyl groups in the region of 3600-3800 cm⁻¹ were evaluated in relation to the area of the two overtone T-O-T stretching vibrations of the framework (1870 and 1981 cm⁻¹). This area was taken as an internal standard, since it is assumed as a measurement of the sample mass reached by the IR-beam.

Pyridine adsorption was used to determine quantitatively the amount of Brønsted and Lewis acid sites. The pyridine measurement was analogous to the hydroxyl measurement just described. The pyridine container was connected to the vacuum cell as well as to the vacuum pump. The connections from the container to the vacuum pump was first evacuated (pyridine slightly boiled) to remove all kind of gasses. The valves were subsequently turned in such a way that a direct connection to the container and the vacuum cell took place for just 10 s. The pyridine was after allowed to desorb at 150°C for at least 12 h but usually until the signal for physisorbed pyridine (1590 cm⁻¹) had completely disappeared. The spectrum was then recorded at 150°C. A second spectrum was obtained at 150°C following an evacuation at 300°C for 20 min. The cell was afterwards opened to fresh air and heated to 500°C to oxidize most of the pyridine that remained on the vacuum cell. As it was the case for the hydroxyl bands, the integrated intensities of the Brønsted (1545 cm⁻¹) and Lewis (1455 cm⁻¹) bands were evaluated in relation to the two overtone T-O-T stretching vibrations of the framework (1870 and 1981 cm⁻¹).
7. CHARACTERIZATION BY MAS NMR

The solid-state $^{29}$Si and $^{27}$Al nuclear magnetic resonance (NMR) spectra were recorded under magic angle spinning (MAS) on a Bruker DSX 500 spectrometer. The $^{29}$Si MAS NMR spectra were obtained at 99.3 MHz with a 7 mm rotors driven by dry air at 5 kHz. All shifts were referred to tetramethylsilane (TMS). A conventional Bloch decay technique and a single-contact cross polarization (CP) from protons were used.

The $^{27}$Al MAS NMR measurements were taken at a Larmor frequency of 130.3 MHz. The probe used was a multinuclear 7 mm CP/MAS probe. All chemical shifts were referred relative to the following liquid external standard: Al(H$_2$O)$_6^{3+}$ from Al(NO$_3$)$_3$$\cdot$$x$H$_2$O. The rotors were spun with dry air at 5 kHz; spinning sidebands could be seen when quadrupolar effects were large. Typically, 1024 Bloch free induction decays (FID) were accumulated using 1 us pulses for the inner $\pm$$1/2$ transition and a 1 s delay between successive pulses. All samples were equilibrated at ambient humidity before packing into the rotors.

$^{27}$Al has an electric quadrupolar moment interacting with the surrounding electric field gradients, leading to a broadening of the spectra by quadrupolar effects. Although MAS can average out the first-order interactions, it is not able to completely cancel the second-order quadrupolar interactions affecting particularly the central $\pm$$1/2$ transition. The use of the 2-dimensional (2D) multi-quantum MAS NMR technique permits to solve this problem. In addition, the method gives high resolution isotropic spectra since the spread of the chemical shifts increases with the order of the multi-quantum transition. The lines of the different species are p times more separated by their isotropic chemical shifts in the multi-quantum dimension than in the classical MAS single-quantum dimension. The multi-quantum spectrum can be described to a first approximation as a spectrum obtained in a „virtual“ magnetic field p times greater than the actual field of the spectrometer.

For the multi-quantum technique, all spectra were recorded with the same number of scans in order to compare the relative intensities of the signals and to estimate the extent of dealumination. The $^{27}$Al 2-dimensional 3-quantum (2D-3Q) MAS NMR spectra were recorded with 196 scans for each experiment and a recycle delay of 1 s. An adequate shearing of the spectrum followed by orthogonal projections produced both the high resolution
(isotropic) spectrum along $v_1$ and the MAS along $v_2$. In addition, shearing of the spectra could be performed in order to align the anisotropic axis parallel to the $v_2$ direction. The result allowed to determine the actual chemical shift and the second-order quadrupolar effect parameter (SOQE) as it could be deduced from the estimation of the quadrupolar induced shift.

It would be advantageous for the determination of the multiple $^{27}$Al species to apply the spectral editing properties of a cross polarization (CP) experiment. However, the spin of interest, in this case $^{27}$Al, is not a spin-$1/2$ nucleus but a spin-$5/2$ nucleus, hence $^{27}$Al has a nonzero nuclear quadrupole moment. CP from a spin-$1/2$ reservoir ($^1$H) to a quadrupolar nonintegral spin nucleus presents another layer of complication in comparison to the CP experiment between pairs of spin-$1/2$ nuclides. Firstly, in CP from a spin-$1/2$ system to an odd integer multiple of $1/2$ spin, the Hartmann-Hahn match condition is modulated by the choice of which transition in the quadrupolar nucleus is to be excited, and the expected gain in signal-to-noise (S/N) ratio is not given simply by the ratio of the gyromagnetic moments for the spins. Secondly, in a $^1$H-$^{27}$Al-CP-experiment the rf power levels is set to perform a selective pulse experiment on the $\pm 1/2$ transition of the $^{27}$Al nucleus. The reduction in the observed signal intensity arises because the selective nature of the transition is violated. Sample spinning renders the quadrupolar splitting, which is function of orientation, time dependent. This time dependence has a profound effect on the spin dynamics involved in the polarization transfer portion of the CP experiment, specifically in the spin-locking condition. Under normal rf conditions, this complication destroys the spinlock and thus severely interferes with the efficiency of the polarization transfer. The result was a significant loss in S/N-ratio with MAS as compared to a static sample.
F. REFERENCES


REFERENCES


REFERENCES


LEBENSLAUF

Persönliche Daten

Name: Dominique Roberge
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Schulbildung

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