Solid acid catalysed conversions of oleochemicals
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CHAPTER 3

Clay Catalysed Dimerisation of Oleic Acid

Abstract

Montmorillonite clay has a unique activity in the dimerisation of unsaturated fatty acids. In Chapter 2, dual site adsorption was proposed to explain this superior catalytic activity. The carboxylic group is thought to co-ordinate to the interlayer metal cations and the activation of the double bond occurs at the tetrahedral substitution site.

In the present work, the hypothesis that reaction takes place in the interlayer of the clay catalyst will further be validated. To this end, experiments with addition of water and ethylene glycol are conducted. Further a range of synthetic clays was synthesised in order to vary systematically the extent of tetrahedral substitution, which was proposed previously to generate the active sites for the reaction of the carbon-carbon double bond.
Introduction

Dimerisation of unsaturated fatty acids is an important process in the oleochemical industry. In this liquid phase batch process not only dimers of fatty acids are formed, but also trimers and isomers of the monomers. All product groups have a number of applications, with, for dimer acids, the most important one being as components in polyamides [1]. A simplified reaction scheme is shown in Figure 3.1. Cis/trans isomerisation, double bond shift, branching, ring formation, aromatisation, hydrogen transfer and lactone formation are side reactions, leading to a variety of compounds during the reaction [2-13]. The resulting ratio between monomers, dimers, and trimers varies within a narrow range and therefore the selectivity of the batch process cannot be manipulated.

Montmorillonite clay has a unique activity in the dimerisation of unsaturated fatty acids. Clays are layered structures and in montmorillonite each layer consists of an octahedral sheet between adjacent tetrahedral sheets. Al$^{3+}$ is the cation in the octahedral layer, with Mg$^{2+}$ as substituent. In the tetrahedral sheet, Si$^{4+}$ is the predominant cation and Al$^{3+}$ the predominant substituent, in the same way as in zeolites. This structure of the layer is typical for the 2:1 pyrophyllite class of clay minerals and is depicted in Figure 3.2.
The extent of substitution in the sheets is different for each (natural) clay, but in montmorillonite substitution in the octahedral position is most abundant. Iron is another element in the montmorillonite structure occupying a small part of the octahedral positions. Substitution leads to an excess negative charge of the layers, which is neutralised by interlayer metal cations and protons. The interlayer metal cations are acidic by polarisation of their hydration shell.

![Layered structure of montmorillonite](image)

Figure 3.2: Layered structure of montmorillonite; no substitutions are shown in this drawing.

Dimerisation is usually performed under 5 to 10 bar steam pressure. The degree of swelling of clays depends on the type of interlayer cations, relative humidity, the charge of the sheets, the origin of the charge and the nature of the molecules adsorbed in the interlayer. Ethylene glycol is often used to test the swelling of clays in XRD-experiments [14, 15].

Only a few studies concerning the dimerisation of unsaturated fatty acids over clays are reported in the literature. Spiteller et al. [2-13] conducted much research on the molecular structures of the products formed in the reaction. Den Otter [16-19] investigated the mechanism of the reaction and the influence of process conditions. He proposed a combined
hydrogen transfer and Diels-Alder mechanism to explain the maximum of around 65 wt.%
dimers that can be found in the clay-catalysed dimerisation of oleic acid. However, this model
neglects the occurrence of hydrogen transfer in dimer and trimer acids, making the model
unrealistic. The presence of saturated dimer acids, as found by Spiteller [8, 9, 12], proves that
dimer acids participate in hydrogen transfer reactions. Moreover, these authors showed that
typical Diels-Alder substitution patterns were absent in the cyclic dimer acids and, therefore,
they proposed a cationic mechanism. The maximum dimer yield is due to hydrogen transfer
leading to saturated unreactive monomers, but hydrogen transfer is not necessarily part of the
dimerisation mechanism itself.

Weiss [20] emphasised the importance of the layered structure, the charge of the clay
layers, and the configuration of the intercalated molecules in the clay catalysed dimerisation
of oleic acid. Unfortunately, no experimental methods, conditions, or references concerning
dimerisation were reported. The only other article providing an explanation for the activity of
montmorillonite clay in oleic acid dimerisation is from Cicel et al.[21]. These authors
proposed that the charge neutralizing interlayer cations, arising from octahedral substitution,
are the active sites in the dimerisation of oleic acid. This is also the case in alkene
dimerisation as reported by Pillai and Ravindranathan in 1994 [22]. Cicel et al. [21] arrived at
this conclusion from the absence of any correlation between structural aspects of the clays,
like octahedral and tetrahedral substitution, and activity. This can be explained, considering
the work in Chapter 2, by the influence of the interlayer distance, which is not taken into
account by Cicel et al. [21]. Moreover, the natural clays used are different not only in the
extent of tetrahedral and octahedral substitution, but also with regard to the presence of
mineral and elemental impurities. This precludes the simple variation of isolated parameters
of the clays.
In Chapter 2, we focused on the nature of the active sites of montmorillonite in the dimerisation of oleic acid. A dual site adsorption was proposed to explain the unique catalytic activity of montmorillonite. The presence of two different acidic sites is the reason that the carboxylic group of oleic acid does not inhibit the dimerisation reaction of oleic acid. The carboxylic group is thought to co-ordinate to the interlayer metal cations, arising from the octahedral substitution, and the activation of the double bond occurs at the tetrahedral substitution site. It is assumed that the reaction takes place in the interlayer of the clay catalyst. In this chapter, this hypothesis, which is previously based on nearly equal activities of different particle size fractions of montmorillonite, is further verified. The absence of marked particle size effects is indeed an indication for predominant reaction in the interlayer, but no proof, since particle size but not crystallite size was varied. Therefore, it still needs to be asserted whether the reaction proceeds in the interlayer. The role of water and other swelling agents in clay catalysed dimerisation is further studied. This role could encompass, apart from swelling of the clay, also hydration of the catalyst surface leading to stronger Brønsted acidity, or hydration of the reactants, when the reaction proceeds over a hydrated intermediate.

Synthetic clays are used to vary systematically the extent of tetrahedral substitution, thus leading to a systematic variation of the active sites as proposed in Chapter 2. Saponite clays, synthesised as described by Vogels et al. [23], are tested as catalysts for oleic acid dimerisation. These clays do not contain Al$^{3+}$ in the octahedral sheet, but divalent metal cations like Zn$^{2+}$ and Mg$^{2+}$. For this reason, the extent of substitution by Al$^{3+}$ in the tetrahedral sheets can be controlled. The variation of the Si/Al ratio may provide further evidence for the role of the tetrahedral substitution sites as the active sites in the dual site adsorption mechanism.
Experimental

Activity Experiments

Experiments are performed in a 150-ml stainless steel autoclave. The autoclave is filled with oleic acid and flushed several times with argon at room temperature, after which heating to reaction temperature is started at 2 bar argon pressure. In contrast to the dimerisation procedure used by others, the catalyst is injected as a slurry with a small part of the reactants only when the reaction temperature is reached. The reaction temperature equals in all cases 528 K. In the presence of water (always 5 wt.% of the initial oleic acid) the reactions are performed under autogenous steam pressure (ca. 8 bar).

Reactants

The 'oleic acid' used (provided by Uniqema) is prepared by hydrolytic splitting of a selectively hydrogenated high oleic sunflower oil. The latter is a mixture of several fatty acids consisting of 85 wt.% oleic and elaidic acid (the trans isomer of oleic acid), 5 wt.% palmitic acid, 6 wt.% stearic acid, and no more than 4 wt.% of poly-unsaturated fatty acids. This mixture is further referred to as oleic acid.

Analysis of reaction products

The reaction products of the oleic acid dimerisation experiments are analysed with a Waters HPLC. An elution gradient of 70/30 acetonitrile-water up to 100% acetonitrile in 16 minutes is used. A subsequent 10 minute run in acetonitrile completes the analysis. The column (C8-reversed phase) is kept at 323 K. The fatty acids are derivatised to 2-naphthacyl esters prior to the HPLC analysis, as described by Cooper et al. [24], to allow UV-detection. Sensitivity factors are determined with pure reactants, except for the dimers and trimers.

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group sensitivity factor is determined for the dimers and trimers, as these represent complex mixtures.

Dimer formation is represented as the molar fraction of the total amount of fatty acids (fraction of FA) that reacts to dimers. No correction for the presence of saturated non-reactive fatty acids is made. The amount of water and ethylene glycol added during reaction is given in weight percentages, where the amount of reactant is taken as 100 %.

**Catalysts**

Montmorillonite (non-activated clay, Grade F160, Engelhard de Meern) is used in the dimerisation and this clay also forms the basis for the preparation of ion-exchanged variants. The ion-exchange procedure consists of overnight stirring in concentrated solutions of nitrates of the relevant cations. Repeated washing with distilled water serves to remove the excess ions and is followed by drying overnight at 353 K.

Saponite clays with several Si/Al rations are prepared by the method described by Vogels et al. [23] from sodium silicate (p.a.: 27 wt.% SiO₂, Merck), urea (99 %) and Al(NO₃)₃.9 H₂O (98+ % from Aldrich). The synthesis is conducted at 363 K during 24 hours. Six washing steps and subsequent centrifuging and decanting, followed by drying at 373 K overnight are performed before use of the catalyst.

**XRD measurements**

XRD experiments are performed on a Philips PW 1710 apparatus, using Co-Kα radiation, under controlled relative humidity (RH) of 10 % and 90 %, or with glycerol as swelling agent. The clays are sedimented on a ceramic tile.
**Elemental analysis**

ICP-AES was used to determine the actual ratio of the elements in the synthetic catalysts on a multichannel Thermo Jarrel Ash ICAP 957 spectrometer, upgraded to ICAP 61.

**Results and Discussion**

**Dimerisation reaction**

The product analysis results vs. reaction time for a typical dimerisation reaction are shown in Figures 3.3-3.5. Spiteller et al. [2-13] conducted an extensive analysis of the different specific compounds formed during the reaction. In this study, we only followed the formation of the different product groups with time. A heating period with concomitant formation of specific products is avoided by injecting the catalyst at the reaction temperature. Although this procedure results in an initial drop of temperature from 528 to 503 K, the original temperature is quickly restored. The HPLC analysis allows us to follow the formation of monomers, dimers, and trimers.

![Graph showing typical dimerisation reaction of oleic acid, formation of dimers and trimers in time; 4 wt.% montmorillonite, T = 528 K, 5 wt.% water, O monomer fraction, □ dimer fraction, Δ trimer fraction.](image.png)

*Figure 3.3: Typical dimerisation reaction of oleic acid, formation of dimers and trimers in time; 4 wt.% montmorillonite, T = 528 K, 5 wt.% water, O monomer fraction, □ dimer fraction, Δ trimer fraction.*
Within the monomer fraction, palmitic acid (in the feed), stearic acid (both present in the feed and formed by hydrogen transfer), isostearic acid, oleic, and elaidic acid can be distinguished. GC-MS analysis confirmed the presence of all products expected. Both Spiteller [7,9,12] and den Otter [17] assumed that elaidic acid is the only active form of 9-10 octadecenoic acid. However, based both on the work of these authors and our work, there is no reason to assume that only elaidic acid is reactive. From these data, one can only conclude that oleic and elaidic acid (and probably regio isomers due to double bond shift) are in relatively fast equilibrium and, therefore, they are plotted together in Figure 3.4.

![Figure 3.4: Typical dimerisation reaction, monomer fraction in time; 4 wt.% montmorillonite, T = 528 K, 5 wt.% water, O oleic and elaidic acid, □ isostearic acid, △ stearic acid.](image)

The dimer acids are separated into three fractions: aromatic, saturated, and cyclic/unsaturated non-cyclic. Figure 3.5 shows that the latter fraction of dimers is formed initially, but diminishes towards the end of the experiment giving both saturated as well as aromatic dimers.

Injection of fresh catalyst after 2 hours of reaction does not lead to further oligomerisation. This is not attributable to the establishment of a thermodynamic equilibrium.
in oligomerisation, since it was verified experimentally that pure dimer and trimer feeds do not react at all to monomers over a fresh catalyst.

![Graph](image1)

**Figure 3.5:** Typical dimerisation reaction, dimer fraction in time; 4 wt.% montmorillonite catalyst, $T = 528$ K, 5 wt.% water, O aromatic dimers, □ cyclic and unsaturated dimers, Δ saturated dimers.

![Graph](image2)

**Figure 3.6:** Typical dimerisation reaction, dimer fraction in time; 4 wt.% catalyst, $T = 528$ K, 5 wt.% water, ♦ used catalyst, □ fresh catalyst.

Although the final concentrations of monomers, dimers, and trimers are reached within 2 hours, side-reactions continue for several hours longer: e.g., hydrogen transfer leads to the formation of aromatic and saturated dimers. Apparently, the catalyst is still active, but all the 'reactive' monomers, i.e. the unsaturated fatty acids, have either oligomerised or
reacted towards saturated monomers. Re-use of the catalyst after filtration, indeed, shows no
loss in activity at all, as it can be seen in Figure 3.6. It is therefore proposed that the
industrially found deactivation of the catalyst can be explained by the formation of poly-
aromatic compounds, due to the poly-unsaturated compounds in the feed or, perhaps, to
specific industrial post-treatment of the product mixture.

**The influence of swelling agents**

Commercially the dimerisation of oleic acid is performed between 513 and 538 K,
with the addition of approximately 5 wt.% water. This leads to a steam pressure in the batch
reactor of around 8 bar. The influence of the water addition is depicted in Figure 3.7. Clearly,
the addition of water leads to a much higher activity of the clay catalyst. As the clay contains
water at room temperature and atmospheric pressure, a drying procedure has also been
performed before reaction. Drying at 413 K overnight leads to an even lower activity of the
montmorillonite clay catalyst, which cannot be ascribed to an irreversible collapse of the clay
structure [25].

![Figure 3.7](image)

*Figure 3.7: Influence of the presence of water on the dimer formation of oleic acid over
montmorillonite: 4 wt.% catalyst, $T = 528 \text{ K}$, △ 5 wt.% water added, □ no water
added, ○ no water added, catalyst dried at 413 K.*

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This is in agreement with earlier findings by den Otter [16, 18] and Schwarz et al. [26], who both found an optimum in water content at comparable steam pressures. The effect is not only an initial effect, as can be seen in Figure 3.8. When extra reactant is injected after 8 hours of reaction, this, in the presence of steam, results in a similar concentration of dimers after another 4 hours of reaction. Again, this shows that the catalyst is still active after reacting for 8 hours. However, if the steam is vented when extra oleic is added again, no more dimerisation activity is detected.

![Figure 3.8: Dimer formation of oleic acid over montmorillonite, after addition of extra oleic acid during reaction; 4 wt.% catalyst, T = 528 K, first in the presence of 5 wt.% water (t = 480 min), then without added water (t = 720 min).](image)

In order to verify the various hypotheses as to the role of water, experiments without water, but with addition of ethylene glycol were performed. Ethylene glycol is often used in XRD experiments to swell the clay. If the function of water is to swell the clay, thereby rendering the clay accessible to the reactants, ethylene glycol could also have a positive effect on the activity of montmorillonite. On the other hand, if the role of water is to hydrate the catalyst surface or the reactants, addition of ethylene glycol is not likely to promote the activity. Ethylene glycol, added to the reaction mixture together with the dried montmorillonite to exclude any influence of water, has a positive effect on the formation of
dimer (Figure 3.9). However, it is found that the drying procedure does not have a large influence on the catalyst activity when ethylene glycol is added, i.e., the effect of swelling by ethylene glycol is dominant (Figure 3.10). Clearly, the experiments with addition of ethylene glycol and water strongly suggest that the reaction takes place in the interlayer.

Figure 3.9: Influence of the addition of ethylene glycol and water on the dimer formation of oleic acid over montmorillonite: 4 wt.% catalyst, $T = 528 \, K$, $\Delta$ 5 wt.% water added, O 5 wt.% ethylene glycol added, catalyst dried at 413 K, ◆ no water added, catalyst dried at 413 K.

Figure 3.10: Influence of the pre-treatment of montmorillonite on the dimer formation of oleic acid with the addition of 5 wt.% ethylene glycol; 4 wt.% catalyst, $T = 528 \, K$, ◆ untreated, O dried overnight at 413 K, Δ dried overnight at 623 K.
Chapter 3

Substitution effects in synthetic clays

It has been proposed in Chapter 2 that the tetrahedral substitution site is the active site for dimerisation of unsaturated fatty acids, with the interlayer metal cations, arising from octahedral substitution, serving as co-ordination sites for the carboxylic group of oleic acid, thus preventing the inhibition of the active sites.

This hypothesis was verified using synthetic saponite clays, allowing the systematic variation of the Si/Al ratio in the tetrahedral sheet. Although in saponites octahedral substitution is absent, vacancies exist in the octahedral sheet, leading also to the presence of interlayer cations. \( \text{Mg}^{2+} \) is used as octahedral cation and as interlayer cation after ion-exchanging the saponite. The saponite with, for instance Si/Al ratio 19 will further be referred to as Mg-Mg-19, with the first symbol representing the interlayer cation and the second the octahedral cation. The results of dimerisation experiments over six Mg-Mg saponites with different Si/Al ratios are compared in Figure 3.11. As expected, the formation of dimers increases with the number of tetrahedral substitution sites, suggesting that these sites are indeed the active sites.

![Figure 3.11: Dimer formation over Mg-Mg-saponites with various Si/Al ratios; 3 wt.\% catalyst, \( T = 528 \) K, 5 wt.\% water, 240 minutes reaction time.](image-url)
The saponite with the highest Al\(^{3+}\) content is the least active. This can have two reasons. The acidity of the tetrahedral sheet can have an optimum as a function of the Si/Al ratio, in accordance with the next nearest neighbour theory developed for zeolites [27]. The amount of acid sites still increases as a function of the degree of substitution in the tetrahedral sheet, but at a certain moment the acid strength of the sites decreases as they on average contain more Al\(^{3+}\) in their second co-ordination shell. An alternative explanation for the lower activity of the saponite with the highest Al content is that at increasing Al content the relative amount of octahedral Al increases and, therefore, the amount of tetrahedral substitution sites decreases. In fact, it may even prove impossible to synthesise the saponite with a high Al content in the tetrahedral sheet, due to the formation of amorphous aluminas and silica-aluminas or incorporation of Al\(^{3+}\) into the octahedral sheet.

X-Ray diffraction patterns of two presumed saponite catalysts are shown in Figure 3.12. The saponite with Zn\(^{2+}\) as octahedral cation clearly shows the (001) reflection, in contrast to the saponite with Mg\(^{2+}\). This is in good agreement with the results of Vogels et al. [23].

![Figure 3.12: XRD of saponites Mg-Mg-5.7 (grey line, right y-axis) and Mg-Zn-5.7 (black line, left y-axis), peaks caused by sample holder omitted.](image-url)
These authors, based on TEM pictures, ascribe this to the low stacking of the layers using Mg\(^{2+}\) as octahedral cation in the synthesis. Saponites with Zn\(^{2+}\) as octahedral cation are composed of platelets consisting of about 10 layers after 12 hours of synthesis.

It is now interesting to compare the results of these saponites with different octahedral cations, providing an indication for the importance of the extent of stacking of the clay for the dimerisation reaction.

**Influence of stacking**

It may be observed from Figure 3.13 that the activity of Mg-Zn-5.7 is higher than that of Mg-Mg-5.7. The difference in activity could be ascribed to a high degree of stacking of the Mg-Zn-saponite. This leads to the conclusion that the layered structure has a positive effect on the reaction of oleic acid, as already proposed by Weiss [20] and discussed in Chapter 2. Weiss claims that oleic acid is oriented perpendicular to the layers, in contrast to oleyl alcohol, which supposedly aligns parallel to the layers and does not react. However, in Chapter 2 is shown that oleyl alcohol does react to the dimer alcohol over montmorillonite, as well as to the corresponding ether. It seems more logical, taking into account the small distances between the layers, that the layered structure forces oleic acid in a parallel orientation towards the sheets. The carboxylic group can adsorb on any site, but the carbon-carbon double bond is still free to be activated at the active site and react with another oleic acid parallel to the chain. According to this structure sensitivity model, adsorption of many oleic acid molecules via the carboxylic group on a non-confined surface could make it impossible for the double bond to adsorb and be activated.
Clay Catalysed Dimerisation of Oleic Acid

Figure 3.13: Formation of dimers over several saponite clays and montmorillonite; 3 wt.% catalyst, $T= 528 \text{ K}$, 5 wt.% water, 240 minutes reaction time; a Montmorillonite, $b$ Ca-Mg-19, $c$ Mg-Mg-19, $d$ Mg-Mg-5.7, $e$ Li-Mg-5.7, $f$ Mg-Zn-5.7.

The difference in activity of Mg-Mg and Mg-Zn saponite could also be attributed to differences in the amount of aluminium in the tetrahedral sheet due to imperfect and incomplete synthesis. Results of Vogels et al. [23, 28] proved that with increasing Al-content the clay structure deviates more and more from a perfect saponite: $\text{Si}_{(8-x)}\text{Al}_{x}\text{Mg}_{6}$. Elemental analysis of the saponites is shown in Table 3.1, confirming the results of Vogels et al. [23].

Table 3.1: ICP results of saponite clays; Si/Al ratio of clay compared with synthesis ratio, $\text{Mg}^{2+}$ compared with perfect saponite structure $\text{Si}_{(8-x)}\text{Al}_{x}\text{Mg}_{6}$

<table>
<thead>
<tr>
<th>Sample Saponite</th>
<th>Si/Al Synthesis</th>
<th>Si (wt.%</th>
<th>Al (wt.%</th>
<th>Mg (wt.%</th>
<th>Li (wt.%</th>
<th>Si/Al (mol/mol)</th>
<th>Mg (wt.%</th>
<th>Si + Al = 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Mg</td>
<td>19.0</td>
<td>24.6</td>
<td>1.3</td>
<td>15.4</td>
<td>18.2</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>19.0</td>
<td>23.6</td>
<td>1.2</td>
<td>14.7</td>
<td>18.3</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>7.0</td>
<td>23.2</td>
<td>2.9</td>
<td>14.8</td>
<td>7.8</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>5.7</td>
<td>22.2</td>
<td>3.5</td>
<td>14.5</td>
<td>6.0</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-Mg</td>
<td>5.7</td>
<td>23.4</td>
<td>3.5</td>
<td>12.5</td>
<td>0.3</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>4.7</td>
<td>23.6</td>
<td>4.9</td>
<td>11.3</td>
<td>4.7</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-Mg</td>
<td>4.7</td>
<td>23.8</td>
<td>5.0</td>
<td>10.6</td>
<td>0.7</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Si/Al ratio aimed for in the catalyst synthesis is confirmed reasonably accurately by the elemental analysis for the synthesised saponites. All $\text{Si}^{4+}$ and $\text{Al}^{3+}$ cations are
apparently used in the synthesis. Whether every Al$^{3+}$ is located in the tetrahedral sheet cannot be concluded from these results, but should be investigated using solid state NMR, as performed by Vogels et al. [23].

The amount of octahedral Mg$^{2+}$ is much lower than expected for perfect saponite clays. Vacancies in the octahedral sheet could explain this, but in the case of Mg-Mg saponites these should be compensated with, again, Mg$^{2+}$ ions. The Li$^+$-exchanged saponites clarify this effect, but clearly the interlayer cations compensate only partially for the shortage of Mg$^{2+}$ in the structure. Octahedral Al$^{3+}$, either in the octahedral layer or in amorphous phases, is therefore assumed to be present. Octahedral Al$^{3+}$ is found, indeed, in saponites prepared in the same way, more or less in proportion with the amount of Al$^{3+}$ incorporated [23, 29].

With Al$^{3+}$ in octahedral and tetrahedral positions as found for low Si/Al ratios, the saponite clay becomes quite similar in structure to montmorillonite. The lower activity of saponites in comparison with the natural montmorillonite clay can have several reasons, such as relatively small interlayer distances, less stacking of the layers or lower number of interlayer cations.

All saponites show similar interlayer distances; about 14.5 Å at 10 % RH, 16 Å at 90% RH, and 18 Å with glycerol. The interlayer distances of the saponite are comparable with active montmorillonite catalysts [1]. Therefore, a small interlayer distance is probably not the cause for the lower activity of saponite compared with montmorillonite in the dimerisation of oleic acid. Both a lower degree of stacking and a lower number of interlayer cations of the saponite are more probable explanations. Variation of interlayer cations in the saponite is conducted in two ways (Figure 13). The Ca-Mg-19 and Mg-Mg-19 saponite are equally active. There is a significant difference in activity between the Li-Mg-5.7 and the
Mg-Mg-5.7. Li$^+$ is able to occupy the octahedral vacancies of the clay at elevated temperatures [30, 31], which could be the cause of the lower activity of the saponite Li-Mg-5.7.

The effect of water on the dimer formation over saponite (Figure 3.14) proved to be similar to the influence of water when montmorillonite is used. Addition of water to the reaction mixture for saponite catalysts leads to an increased dimerisation activity, in a similar way as observed for montmorillonite.

![Figure 3.14: Effect of water addition on the dimerisation activity of saponite Mg-Mg-7 (3 wt.% and montmorillonite (4 wt.%), 5 wt.% water or no water added, T = 528 K.](image-url)
Concluding Remarks

Montmorillonite clay used as the catalyst for dimerisation of oleic acid is not deactivated during this reaction and may be re-used.

Both ethylene glycol and water have a positive effect on the dimerisation activity of montmorillonite clay. Hydration of the surface or hydration of the reactants cannot explain this similarity and therefore the impact of water on the activity can only be attributed to swelling of the clay. This is in agreement with findings in Chapter 2, where it was shown that the dimerisation activity of several ion-exchanged montmorillonites strongly depends on the interlayer distance. From these results, it may be concluded that dimerisation of unsaturated fatty acids over montmorillonite takes place predominantly in the interlayer.

Variation of the degree of tetrahedral substitution shows that up to 20 % Al the activity of the saponite increases with the number of tetrahedral substitution sites. This is in agreement with the earlier proposal that these sites are the active sites in the dimerisation of oleic acid. Still, the interlayer cations are proposed to play a vital role by preventing the inhibition of the active sites by the carboxylic group of oleic acid. The lower amount of interlayer cations and the lower degree of stacking, *i.e.* a house of cards structure, are possible explanations for the lower activity of saponite clay catalysts, compared with montmorillonite.
References


