Active sites in the clay catalysed dimerisation of oleic acid

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Abstract

The superior catalytic activity of montmorillonite clay in the dimerisation of unsaturated fatty acids is not well understood. In this paper we describe investigations into the relative importance of the various acid sites as well as structural and textural parameters of montmorillonite for the dimerisation of oleic acid. It is shown that reaction in the interlamellar space dominates the oleic acid dimerisation. The active site is the tetrahedral substitution site, and the influence of the type of interlayer cation on the activity of montmorillonite is explained in terms of its effect on the interlayer distance. Model catalysts with mesopores and tetrahedral substitution sites do not show any activity in oleic acid dimerisation. A dual site adsorption of oleic acid, i.e., requiring the presence of both interlayer cations (arising from octahedral substitution) and tetrahedral substitution sites, is proposed as explanation for the superior activity of montmorillonite. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Dimerisation of unsaturated fatty acids is a liquid phase batch process. Montmorillonite clay is much employed as heterogeneous catalyst in this reaction. The major product groups are dimers, trimers, and isostearic acid. Dimers and trimers have several applications [1], the most important ones being as components in polyamides, e.g., in hot melt adhesives, epoxy-coatings and flexographic printing inks. The monomer fraction of the product is applied in lubricants or cosmetics.

The main reaction pathways in case of oleic acid dimerisation are depicted in Fig. 1. How-

ever, due to the occurrence of many side-reactions the three product groups each consist of numerous compounds. This is even more so when a natural (industrial) feed, consisting of a variety of fatty acids, is employed. The predominant side reactions are hydrogen transfer, double bond shift, *cis/trans* isomerisation, and chain branching [2,3]. Problems in analysis and interpretation of the complex reaction mixtures were partly avoided in this study, by using high oleic acid sunflower oil as reactant. This 'oleic acid' contains less than 4% of poly-unsaturated fatty acids (linoleic and linolenic acid).

Homogeneous catalysts have been used in dimerisation, but are only active with the methyl esters of the fatty acids as reactants [4]. Dimers of fatty acids can be made using radical initia-
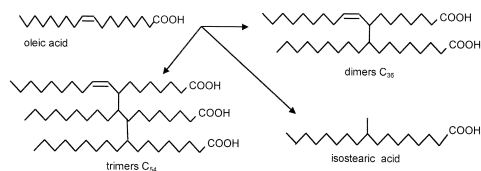
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Fig. 1. Dimerisation reaction scheme.

tion [5], but this leads to an unfavourably high amount of trimers and higher oligomers, compared with the montmorillonite clay catalysed process. Montmorillonite clay is by far the most active heterogeneous catalyst found in scientific and patent literature. The superior catalytic activity of montmorillonite clay in the dimerisation of fatty acids is not well understood. As a first step towards the understanding of this unique activity, a study to elucidate the nature of the active sites in this reaction is conducted.

Montmorillonite is a 2:1 phyllosilicate, which is a structural class of clays. Clays are layered structures and in case of 2:1 phyllosilicates these layers consist of an octahedral sheet between two tetrahedral sheets. The 2:1 phyllosilicates are divided into di- and trioctahedral phyllosilicates. In trioctahedral 2:1 phyllosilicates, Al^{3+}-cations occupy two out of three octahedral positions. In dioctahedral phyllosilicates all octahedral positions are occupied by divalent metal cations. The tetrahedral sheets consist of SiO_4^{2-}-tetrahedra. In Fig. 2 the structure of a perfect trioctahedral phyllosilicate (pyrophillite) is shown.

Montmorillonite is a trioctahedral phyllosilicate like pyrophillite, but contains isomorphous substitution sites. Mg^{2+} substitutes Al^{3+} (~ 1 out of 4 Al^{3+}) in the octahedral sheet and Al^{3+}
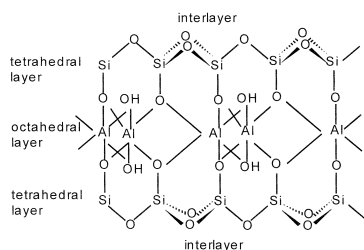
substitutes Si^{4+} (~ 1 out of 25 Si^{4+}) in the tetrahedral sheet [6,7]. The extent of substitution in both sheets is different for each (natural) clay. As iron impurities and the presence of other minerals cause even more variation in natural clays, differences in the catalytic activity of various natural clays should be interpreted cautiously and the use of natural clays avoided whenever possible. Instead, the use of synthetic clays is preferable.

Protons and metal cations in the interlamellar space balance the negative charge of the layers, originating from octahedral and tetrahedral isomorphous substitution. Interlayer metal cations are easily hydrated and can, therefore, cause the clay to swell [8]. Swelling may proceed up to the point where four or more layers of water are accommodated in the interlayer, depending on the type of interlayer cation, relative humidity, and the charge of the sheets [9,10]. Other polar fluids cause swelling of the clay as well, for instance ethylene glycol is often used to test the swelling of clays in XRD experiments [9,11]. Even benzene is known to penetrate the interlayer of montmorillonite [11].

Unlike many other reactions catalysed by clays (as Friedel–Crafts alkylations [12]), no acid activation procedure is used to increase the acidity of the montmorillonite. The acidity of non-activated montmorillonite clay is found to stem from various sources [13–17]:

1. Interlayer metal cations, neutralising the negative charge of the octahedral layer, give Brønsted acidity due to polarisation of their hydration shell.
2. Tetrahedral substitutions lead to acid sites in the interlayer, by neutralisation of the resulting excess negative charge with protons or metal cations.
3. Octahedral sites at the external surface of the clay particles, i.e., located at the edges of the sheets.
4. Interlayer metal cations, acting directly as Lewis acids.

Only a few studies concerning the dimerisation of unsaturated fatty acids over clays were

Fig. 2. Structure of a trioctahedral 2:1 phyllosilicate.

reported in the literature, and almost none about the active sites of the clay. Den Otter [2,18,19] and Heynen et al. [20] investigated the mechanism of the reaction and the influence of the process conditions. The latter was studied by Schwarz et al. [21] and Brát et al. [22] as well. Möhring and Spiteller [3,23], Adelhardt and Spiteller [24], Link and Spiteller [25–27] and Brütting and Spiteller [28] conducted much research into the exact structure of the products formed in the reaction. They proposed a cationic mechanism, instead of a combined hydrogen transfer/Diels–Alder mechanism, as proposed by den Otter. Weiss [29] emphasises the importance of the layered structure, the charge of the clay layers, and the configuration of the intercalated molecules. Unfortunately, no experimental methods, conditions, or references concerning dimerisation are reported in this article.

Cicel et al. [6] studied oleic acid dimerisation using montmorillonite exchanged with several metal cations. From the observed minor differences in activities they concluded that the interlayer cations, via polarisation of co-ordinated water, form the active centres. However, in our opinion such a limited experimental parameter variation cannot provide conclusive evidence for this hypothesis in such a complex reaction system.

In this paper we describe investigations into the relative importance of the various acid sites and structural and textural parameters of montmorillonite for the dimerisation of oleic acid.

2. Experimental

2.1. Activity experiments

Experiments are performed in a 150 ml stainless steel autoclave. The autoclave is flushed several times with argon at room temperature before reaction and heating to reaction temperature is started at 2 bar argon pressure. In contrast to other studies, the catalyst is injected as a slurry with a small part of the reactants only

when the reaction temperature is reached. This leads to a better defined starting point of the reaction. The injection of catalyst leads to a small temperature drop, but within 3 min the reaction temperature is re-established. The reaction temperature is in all cases 528 K. In the presence of water (always 5 wt.%) the reactions are performed at autogenous steam pressure.

2.2. Reactants

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

1-Dodecene and technical oleyl alcohol are obtained from Aldrich, palmitic acid from Merck. The 9-octadecene is prepared from 1-decene (Aldrich) using metathesis. The metathesis reaction is performed at room temperature using 25 wt.% of high alumina silica alumina (AKZO Nobel) and 0.5 wt.% tetrabutyltin as catalyst. Methyl oleate is prepared from the oleic acid mentioned above, using the method described by Harrison et al. [30]. The acid value of the methyl oleate used is < 1 mg KOH/g methyl oleate.

2.3. Analysis of reaction products

The reaction products of the oleic acid dimerisation experiments are analysed with a Waters HPLC. A gradient of 70/30 acetonitrile–water up to 100% acetonitrile in 16 min is used. A subsequent 10 min run in acetonitrile completes the analysis. The column (C8-reversed phase) is kept at 323 K. The fatty acids were previously derivatised to 2-naphtacyl esters, as described by Cooper and Anders [31], in order to be able to use UV-detection. Sensitivity factors are determined with pure reactants, ex-

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

The products of the reactions with alkenes, oleyl alcohol and methyl oleate are analysed by gas chromatography. The Carlo–Erba GC contains a DB-1 megabore column (J & W) and a FID detector.

2.4. Catalysts

The same montmorillonite (non-activated clay, Grade F160, Engelhard de Meern) is used in the clay catalysed reactions and forms the basis in the preparation of ion-exchanged clays and acid activated montmorillonite (Grade F160, activated clay, Engelhard de Meern). The ion-exchange procedure consists of overnight stirring in concentrated solutions of nitrates of several cations and drying overnight at 353 K. Repeated washing with distilled water serves to remove the excess ions.

Several silica–aluminas are obtained from AKZO: SALAL, SAHA, SALAH, SALA-10, and SiAl-KDC. Laponite RD is obtained from Laporte Industries, SiO_2 S980 A from Shell, γ-alumina CK-300 from AKZO, and the MCM-41 (Si/Al = 16) is prepared as described by Beck et al. [32] and Janicke et al. [33]. The Al^{3+} source for the latter is aluminium isopropoxide.

2.5. XRD measurements

XRD experiments are performed on a Philips PW 1710 apparatus, using Co–Kα radiation, under controlled relative humidity of 90%RH. The clays are sedimented on ceramic tile.

3. Results and discussion

A standard dimerisation experiment with 8 wt.% montmorillonite and 5 wt.% water is presented in Fig. 3. Although the final concentrations of monomers, dimers and trimers are
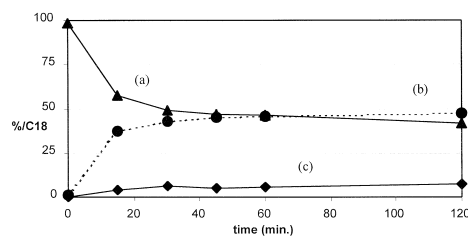

Fig. 3. Standard dimerisation experiment: 8 wt.% montmorillonite, oleic acid, 5 wt.% H_2O; (— ▲ —) monomer fraction, (· · · ● · · ·) dimers, and (— ◆ —) trimers.

reached within 2 h, side-reactions continue for several hours longer: e.g., hydrogen transfer leads to formation of aromatic and saturated dimers. Injection of fresh catalyst after 2 h of reaction does not lead to further oligomerisation. This is not attributable to the establishment of a thermodynamic equilibrium in oligomerisation: separated dimers and trimers do not react at all back to monomers with fresh catalyst. Therefore, it seems that all oleic and elaidic acid reacts to oligomers or monomers, unreactive towards oligomerisation, within the first 2 h of this experiment.

Sources of acidity of the montmorillonite clay may originate both from the interlamellar space (interlayer) and from the external surface of the clay particles. To find out whether the reaction is dominated by interlayer or external surface area activity, particle size fractions of the same montmorillonite clay were tested. The sieve fraction of 45–180 μm and the fraction < 45 μm have the same dimerisation activity (see Fig. 4). In view of the widely differing external surface area and comparable internal surface area per unit of weight, this result is a first
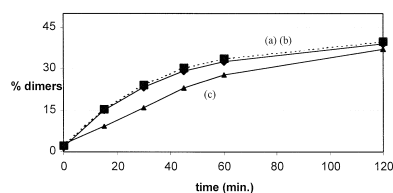

Fig. 4. Influence of clay particle size on the montmorillonite catalysed oleic acid dimerisation: 1.75 wt.% montmorillonite, 5 wt.% H_2O; sieve fractions; (— ◆ —) < 45 μm, (· · · ■ · · ·) 45–180 μm, and (— ▲ —) > 180 μm.

indication that the reaction mainly occurs at the interlayer. Other indications pointing to the same conclusion will be discussed below. The fraction of particles larger than 180 μm is slightly less active, possibly due to mass transfer limitations. Reaction directly at octahedral sites can, therefore, not be mainly responsible for the activity of the montmorillonite clay, as these sites are only present at the external surface, at the edges of the sheets. Interlayer cations, arising from octahedral substitution, and tetrahedral substitution sites are more likely active sites, because these sites exist in the interlamellar space.

Laponite, a synthetic clay from Laporte Industries resembling hectorite, contains octahedral substitution sites (and thus interlayer cations), but no tetrahedral substitution sites. Surprisingly, this catalyst was not active in oleic acid dimerisation (see Table 1). It is noteworthy that these interlayer cations, present in the laponite (not active in oleic acid dimerisation), are proposed as active sites in the dimerisation of oleic acid by Cicel et al. [6]. XRD experiments show comparable interlayer distances for the laponite and montmorillonite (Table 1). The laponite is tested as its Mg^{2+}-exchanged form, because the Mg^{2+}-montmorillonite is quite active in oleic acid dimerisation (Fig. 5).

The above mentioned data lead us to conclude that tetrahedral substitution is necessary for any dimerisation of oleic acid to occur. The presence of interlayer cations as such in a layered structure is not sufficient for oleic acid dimerisation. However, the laponite is active in 1-dodecene dimerisation, its activity being comparable with the activity of the montmorillonite clay. Apparently, the carboxylic group of oleic acid inhibits the reaction of the double bond (C=C) of oleic acid, probably by strong competitive adsorption of this carboxylic group at the acidic sites of the laponite.

Table 1
Oleic acid, 1-dodecene, and 9-octadecene dimerisation over various catalysts

| Catalyst	d_{100} (Å) 90%RH	wt.% catalyst	Reactant	Reaction time (min)	% dimers	Acid value (mg KOH/g)
Montmorillonite	15.4	8	oleic acid	240	50	183
		4	1-dodecene	240	20	
		8	oleic acid	30	43	
Mg^{2+}-laponite	15.9	6	oleic acid	240	< 1	
		4	1-dodecene	240	17	
SiO_2		8	oleic acid	120	4	
		8	1-dodecene	60	< 1	
SA-LAL		8	oleic acid	120	9	154
		8	1-dodecene	60	9	
SA-HA		8	oleic acid	120	5	149
		6	1-dodecene	60	47	
		8	9-octadecene	120	20	
SA-KDC		8	oleic acid	30	4	168
		8	1-dodecene	60	41	
γ-Al_2O_3		8	oleic acid	120	< 1	
		8	1-dodecene	60	< 1	
MCM-41 (Si/Al = 16)		4	oleic acid	120	< 1	158
		4	1-dodecene	60	30	
Li^+-montmorillonite, immersed in H_2O	indeterminable	1.5	oleic acid	120	41	
Li^+-montmorillonite, standard procedure	indeterminable	1.5	oleic acid	120	41	
Acid-activated montmorillonite	indeterminable	8	oleic acid	30	26	
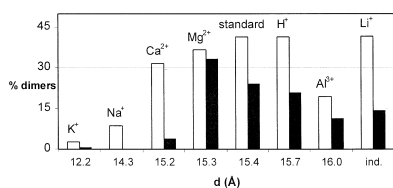
Fig. 5. Effect of interlayer cations on interlayer distance and dimerisation activity: 1.5 wt.% ion-exchanged montmorillonite, 5 wt.% H_2O; □ oleic acid, ■ 1-dodecene.

Although the acidity connected with the interlayer cations clearly is not by itself sufficient for oligomerisation activity, it is nevertheless of interest to study the impact of the type of interlayer cation (i.e., systematic variation of the strength of one type of acid sites) on dimerisation activity. The influence on the dimerisation rate of oleic acid is found to be large (Fig. 5), but it is not proportional to the acidity of the interlayer cations. According to the literature, the order of acidity, due to polarisation of water, of the interlayer cations is: $Al^{3+} > Mg^{2+} \gg Ca^{2+} \approx Li^+ > Na^+ > K^+$ [15]. However, Ca^{2+}-montmorillonite is almost as active as the Mg^{2+}-montmorillonite and Li^+-montmorillonite even proves to be the most active form. Obviously, other factors underlie the observed differences in activities of these exchanged clays.

The influence of the type of interlayer cation on the swelling of the clay is frequently mentioned in the literature [9,34]. The degree of swelling may have an effect on the rate of intercalation of oleic acid and, therefore, on the rate of dimerisation. XRD measurements of all ion-exchanged clays were performed under controlled relative humidity (90%RH) and the interlayer distances were calculated using the d_{100} reflection. The height of the TOT-layers is 9.1 Å [35], and this value can be subtracted from the d-values found in Fig. 5 to give the distance between the layers.

The rate of oleic acid dimerisation clearly depends on the type of interlayer cation through its influence on the interlayer distance and not directly because of its acidity. Al^{3+}-montmorillonite is the only ion-exchanged clay with a different behaviour: a relatively large interlayer distance and low conversion of oleic acid. This can be explained by formation of solid aluminium hydroxides inside the interlayer, which is known to occur in Al^{3+}-exchanged clays under hydrothermal conditions [36]. This may block the interlayer for the intercalation and diffusion of the reactants and products, resulting in a lower reaction rate. The dependence of activity on the nature of the interlayer cations, again, indicates that the reaction proceeds predominantly in the interlayer and not at the external surface area.

The results of the experiments with the laponite suggest that the interlayer cations, arising from octahedral substitution, are active sites in 1-dodecene dimerisation, but not in oleic acid dimerisation. The activity in oleic acid dimerisation depends on the type of interlayer cation only through its influence on the swelling of the clay. Since in 1-dodecene dimerisation the interlayer cations are the active sites, the type of interlayer cation should have an effect on the rate of 1-dodecene dimerisation via both swelling and acidity of the clay. Different relationships between activity and the type of cation are, therefore, expected for oleic acid and for 1-dodecene dimerisation. From Fig. 5 it can be seen that this is indeed the case: the acidic Mg^{2+}-montmorillonite, possessing only average activity in oleic acid dimerisation, is by far the most active clay in 1-dodecene dimerisation. Moreover, Li^+-montmorillonite, which has the highest activity in oleic acid dimerisation, is not very active in 1-dodecene dimerisation. The results of the 1-dodecene experiments agree very well with the results obtained by Muthukumaru Pillai and Ravindranathan in 1-decene dimerisation [37], as they conclude as well that in alkene dimerisation the activity of montmorillonite depends on the acid strength of the interlayer cations.

If the only function of interlayer cations, related to octahedral substitutions, in oleic acid dimerisation is to provide sufficient interlayer spacing and tetrahedral substitution sites are the

actual active sites, mesoporous catalysts containing this latter type of sites should show activity. Hence, both MCM-41 (Si/Al = 16) and several silica–aluminas were tested in the dimerisation of oleic acid, but none were found to be active (Table 1). Apparently either the presence of tetrahedral substitution sites is not sufficient for oleic acid dimerisation activity, or the tetrahedral substitution sites of the clay are of a different nature than the tetrahedral substitution sites in the model catalysts tested. For the silica–aluminas the latter could very well be true: they all had a lower Si/Al ratio than the tetrahedral sheet of montmorillonite, leading to lower acid strength of the active sites in silica–aluminas. The formation of alumina-ensembles at the surface of the silica–aluminas may be another difference with the active sites of the clay. Neither of these arguments hold for MCM-41 with a Si/Al ratio of 16. This ratio is comparable to the ratio in the tetrahedral sheet of natural montmorillonite clays and the formation of alumina ensembles is not expected to occur. A different reason for the high activity of montmorillonite, with respect to MCM-41 (Si/Al = 16), in oleic acid dimerisation should, therefore, exist.

Although the presence of tetrahedral substitution sites is not sufficient for dimerisation of oleic acid, 1-dodecene dimerisation is catalysed by MCM-41 (Si/Al = 16) and silica–aluminas as evidenced by Table 1. An experiment with 9-octadecene (having a similar carbon chain length and position of the double bond as oleic acid) with silica–alumina (SAHA) proves that the different activity of silica–aluminas in oleic acid and 1-dodecene dimerisation is not explained only by the different position of the double bond and different chain length of oleic acid and 1-dodecene. The decrease in acid value represents the amount of soap formed during oleic acid dimerisation (Table 1). As the oleic acid feed has an acid value of 194 mg KOH/g oleic acid, the data presented strongly suggest that the carboxylic group of the oleic acid inhibits the dimerisation of oleic acid over silica–alumina by competitive adsorption and soap formation with the Al^{3+}-ions of the catalyst.

To verify this hypothesis, an 1-dodecene dimerisation experiment, using silica–alumina catalyst and adding 5 wt.% saturated fatty acid (palmitic acid), was performed (Fig. 6). The conversion of the 1-dodecene is seen to decrease significantly in the presence of the saturated fatty acid. Hence, carboxylic groups seem to block the active sites of the silica–aluminas, but not the active sites of montmorillonite clay.

Therefore, the influence of this carboxylic and other functional groups in the clay catalysed dimerisation were studied further. An alkene, alcohol and methyl ester analogous to oleic acid have been used. All experiments are performed with and without the addition of water, and are shown in Figs. 7 and 8

Oleyl alcohol reacts with a comparable rate to oleic acid, but a substantial part of the dimers of oleyl alcohol results from etherification, instead of dimerisation at the double bond. Both products were found using Field Emission Mass Spectrometry. This result contradicts the results reported by Weiss [29], who claimed that montmorillonite is not active in oleyl alcohol dimerisation. Polar groups (especially the carboxylic group) enhance the dimerisation rate on the clay catalyst (Figs. 7 and 8). As is apparent from Fig. 7, the oleic acid reacts more rapidly over the montmorillonite compared with its analogous alkene. Probably the intercalation of the
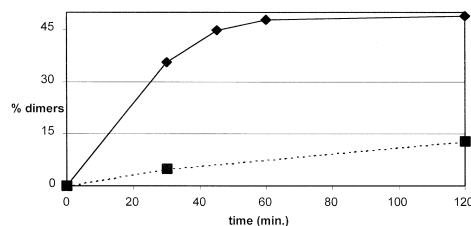

Fig. 6. Effect of the addition of 5 wt.% palmitic acid on dimerisation of 1-dodecene: — ♦ — 6 wt.% SAHA, · · · · ■ · · · · 8 wt.% SAHA + 5 wt.% palmitic acid.
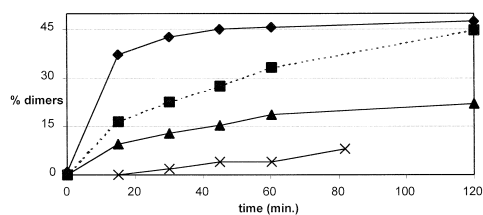
Fig. 7. Dimerisation of various reactants as a function of time: 5 wt.% water, 8 wt.% montmorillonite; — ◆ — oleic acid, ···· ■ ···· oleyl alcohol, — ▲ — methyl oleate, —x— 9-octadecene.

Fig. 9. Effect of the addition of 5 wt.% palmitic acid on clay catalysed dimerisation of methyl oleate: 8 wt.% montmorillonite; ···· ■ ···· methyl oleate + 5 wt.% palmitic acid, — ▲ — methyl oleate.

reactants into the initially hydrophilic clay is facilitated by the presence of the polar group. This is, again, an indication of the reaction being dominated by the interlayer.

The importance of the polar group becomes even clearer, when 5 wt.% palmitic acid is added to a reaction of methyl oleate, as shown in Fig. 9. Methyl oleate itself seems not to be able to penetrate into the interlayer, but in the presence of palmitic acid the clay becomes increasingly hydrophobic through intercalation of the palmitic acid. At this point the reaction of methyl oleate is enhanced by easier intercalation of this species. The enhanced dimerisation of methyl oleate in the presence of water (Fig. 7) can be explained by partial hydrolysis of the methyl ester to oleic acid (the acid value of the product is 67 mg KOH/g), which should have the same effect as the addition of palmitic acid. Notice that the effect of the addition of the palmitic acid in the clay catalysed dimerisation of methyl oleate is opposite to the effect in the silica–alumina catalysed reaction of 1-dodecene (Fig. 6).
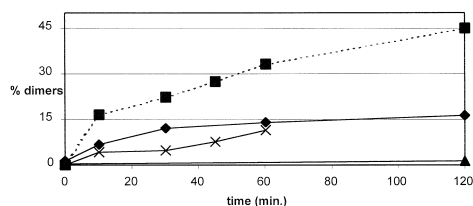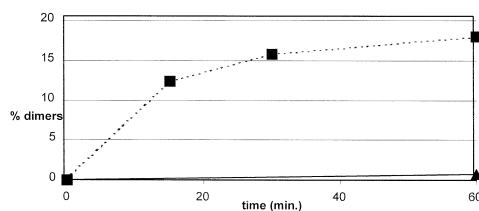

Fig. 8. Dimerisation of various reactants as a function of time: without addition of water, 8 wt.% montmorillonite; — ◆ — oleic acid, ···· ■ ···· oleyl alcohol, — ▲ — methyl oleate, —x— 1-dodecene.

The effect of addition of water on the dimerisation rate of oleic acid is large and can be explained by the increased interlayer distance upon swelling of the clay with water, leading to increased intercalation and reaction of oleic acid. This effect is in accordance with the results of ion-exchanged clays, for which the swelling of the clay is found to be the important factor as well.

In conclusion, model catalysts with either interlayer cations (arising from octahedral substitution) or tetrahedral substitution sites as active sites, have been tested. Both types of model catalysts are active in 1-dodecene dimerisation, but show no activity at all in the dimerisation of oleic acid. Probably, the carboxylic group inhibits the activation of the double bond at the active sites by strong competitive adsorption. The only exception is the montmorillonite clay, which contains both types of sites in a layered structure.

One possible explanation for this exception is that the layered structure of the clay forces the reactants into an adsorption mode parallel to the tetrahedral sheet, in which the double bond can adsorb at the active sites (the tetrahedral substitution sites). In a non-layered material the adsorption might be preferentially via the carboxylic group with the molecule perpendicular to the surface, inhibiting the activation of the double bond. Another hypothesis is that the interlayer cations, arising from octahedral substitution in the clay, bind the carboxylic groups and thereby prevent the inhibition of the tetrahedral substitution sites of the clay. The remainder

of the discussion in this paper is an attempt to verify either one of these two hypotheses to explain the superiority of montmorillonite clay.

Li^+-montmorillonite, which gives the highest conversion of the ion-exchanged clays, is known to swell to complete delamination in water [9]. Already at 90% RH, there is no distinct maximum of the d_{100} peak left, in contrast to all other ion-exchanged montmorillonites. XRD data of Li^+- and Mg^{2+}-montmorillonite are shown in Fig. 10. The Li^+-montmorillonite, immersed in water before reaction, catalyses the oleic acid dimerisation just as well as in a normal experiment (see Table 1), without prior mixing of clay and water. An optimum in interlayer distance may be anticipated if the parallel adsorption is the reason of the superior activity of the clay. The behaviour of the Li^+-montmorillonite seems to contradict this. The necessity of dual site adsorption of oleic acid, i.e., the presence of interlayer cations and tetrahedral substitution sites, seems therefore the more likely explanation of the high activity of montmorillonite. However, the interlayer distances cannot be measured under reaction conditions, and, therefore, proof of complete delamination during reaction was not obtained.

Another aspect pointing in the same direction is the fact that acid activated montmorillonite gives less, but still considerable, conversion (see Table 1) of oleic acid compared with the same non-activated clay. XRD measurements (Fig. 10) hardly show a d_{100} peak in the acid activated clay. The lower activity of the acid activated clay could thus be attributed to either

Fig. 10. XRD of (a) Li^+-, (b) acid activated-, and (c) Mg^{2+}-montmorillonite at 90% RH.

delamination, if the layered structure is needed, or to leaching of tetrahedral aluminium [7,38], which destroys the active sites. Again, a proper distinction between the two hypotheses is as yet impossible.

Additional arguments can be derived from the soap formation during oleic acid dimerisation (Table 1), which occurs readily in MCM-41 ($Si/Al = 16$) and silica–aluminas, but occurs significantly less in case of a montmorillonite catalysed reaction, even after longer reaction times and with high catalyst loading. This indicates the only weak interaction between the carboxylic group and the tetrahedral substitution sites of the montmorillonite. If the adsorption mode, due to the layered structure, is the only crucial factor next to tetrahedral substitution, there seems to be no reason for a weaker interaction of the carboxylic group with the active sites of the clay, as compared with for instance the MCM-41 catalyst. However, the presence of interlayer cations, binding the carboxylic groups, explains the absence of soap formation in the montmorillonite catalysed reaction. Therefore, interlayer cations seem to be crucial to oleic acid dimerisation activity (next to tetrahedral substitution), preventing the inhibition of the active sites by the carboxylic group of oleic acid.

4. Concluding remarks

Montmorillonite clays are layered structures, each layer consisting of an octahedral sheet between two tetrahedral sheets. Isomorphous substitution in both the tetrahedral and the octahedral sheets leads to an excess negative charge of the layers, which is compensated by interlayer metal cations and protons, leading to different acid sites. The relative importance of the various acid sites, as well as the structural and textural parameters of montmorillonite, in the dimerisation of oleic acid was investigated.

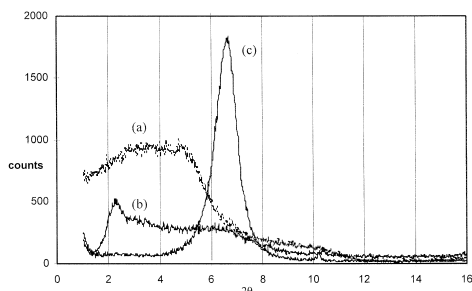A variety of arguments, strongly suggesting that the activity of montmorillonite clay for

oleic acid dimerisation is dominated by reaction in the interlamellar space, has been presented. Results of experiments with laponite, a synthetic clay with octahedral substitution, demonstrate that tetrahedral substitution is a prerequisite for dimerisation of oleic acid. This is not true for 1-dodecene dimerisation, which is readily catalysed by Mg^{2+}-laponite.

Although the type of interlayer cation has a large effect on the rate of oleic acid dimerisation, the dependence of the activity of montmorillonite on the type of interlayer cation in this case is different from that in 1-dodecene dimerisation. If interlayer cations were the active sites in oleic acid dimerisation (as they are in 1-dodecene dimerisation) the activity of montmorillonite in oleic acid and 1-dodecene dimerisation would be expected to depend in a similar way on the type of interlayer cation, in proportion to the acidity of their hydration sphere. Therefore, in oleic acid dimerisation the tetrahedral substitution site must be the active site and the influence of the type of interlayer cation on the activity of montmorillonite is explained by its effect on the interlayer distance. The addition of water enhances the dimerisation rate, and this can also be explained by increased swelling of the clay.

Various silica–alumina type catalysts, i.e., with tetrahedral substitution sites as active sites, have been tested. These catalysts are active in 1-dodecene dimerisation, but not active at all in oleic acid dimerisation. The carboxylic group of oleic acid inhibits the activation of the double bond at the active sites of all catalysts tested by strong competitive adsorption, except for the active sites of the montmorillonite clay. Moreover, when oleic acid dimerisation in montmorillonite is compared for instance with its analogous methyl ester and alkene, the carboxylic group even increases the dimerisation rate at the double bond, probably by enhancing the intercalation of the reactants in the hydrophilic clay.

A possible explanation for this exception is that the layered structure of the clay forces the reactants into an adsorption mode parallel to the tetrahedral sheet, in which the double bond is able to adsorb at the active sites. Another hypothesis is the presence of interlayer cations, arising from octahedral substitution, binding the carboxylic groups and thus preventing the inhibition of the tetrahedral sites of the clay. The second hypothesis is preferred by the authors, as the absence of soap formation during montmorillonite catalysed reaction can be understood only with this explanation of the superiority of the montmorillonite.

Acknowledgements

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