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Hydrogenation of edible oils and fats

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5. Adsorption



Adsorption of reactants (and products) is a key prerequisite of heterogeneously catalyzed reactions. As was shown in Chapter 3, different adsorption strengths of poly- and monounsaturated fatty acids may explain observed reaction selectivities. However, quantitative evidence on different adsorption strengths have not been established yet. Therefore, we have used two types of experiments for an independent determination (i.e., without using reaction data) of adsorption of double bonds on nickel catalysts: the retention times of the tracer pulse column experiments (from Chapter 4) and a series of batch mass-balance experiments with a custom made small autoclave.

5.1. Introduction

Data on adsorption of FAMEs on heterogeneous catalysts are scarce; Table 5.1 lists the range of adsorption enthalpies obtained from literature. Lidefelt (1983) performed gas chromatography experiments in packed columns using saturated and unsaturated FAMEs and calculated comparable adsorption enthalpies for mono- and diunsaturated FAME from the mean residence time. The interaction of saturated FAME on silica, a commonly used support for hydrogenation catalysts, was investigated by Mills and Hockey (1975). Under hydrogenation conditions, saturated FAME usually is the solvent. Then the adsorption enthalpy of unsaturated FAMEs is obtained relative to the adsorption enthalpy of saturated FAME (Table 5.1, Gut et al., 1979; Chapter 2 and 3). The ambiguity of the limited data of liquid phase adsorption of fatty acids (Table 5.1) indicate the necessity of further research into adsorption phenomena (Veldsink et al., 1997).

Table 5.1. Adsorption Enthalpies of Saturated (S), Mono- (M) and Diunsaturated (D) FAME from Literature.

source	solvent ^a	adsorbens ^b	$\Delta\hat{H}_S^a$ kJ/mol	$\Delta\hat{H}_M^a$ kJ/mol	$\Delta\hat{H}_D^a$ kJ/mol
nonreactive conditions					
Lidefelt, 1983	nitrogen	Ni-Al		-85	-94
Mills and Hockey, 1975	benzene	Si	-35		
	CCl ₄	Si	-52		
under hydrogenation conditions					
Gut et al., 1979	S	Ni-Si		-28	-35
Chapter 2	S	Ni-Si		0	
Chapter 3	S	Ni-Si		0	13

^a Adsorption enthalpy relative to solvent. ^b Si = silica particles, Ni-Al = nickel on alumina catalyst.

The adsorption of saturated versus unsaturated FAME on supported nickel catalysts can be evaluated from Table 5.1. In adsorption experiments under nonreactive conditions, both saturated and unsaturated FAMEs show large adsorption enthalpies, which implies a strong interaction of the methyl ester group with the catalyst (support). This was also suggested by Mendioroz and Muñoz (1990) and by Rodrigo et al. (1992). As a result, adsorption parameters obtained from hydrogenation experiments are much smaller, because these values are relative to saturated FAME (see Table 5.1). Therefore, the most direct way to investigate the adsorption of double bonds on nickel is to use a mixture of unsaturated and saturated methyl esters with a pure (Raney) nickel catalyst, to avoid the influence of the carrier.

Ideally, adsorption parameters should be measured under reaction conditions, to obtain relevant information for kinetic rate expressions (Weller, 1992). Therefore, relating adsorption parameters under typical reaction conditions to data from surface science studies (for nickel catalysts: e.g., Machiels and Anderson, 1979; Kinza et al., 1985; Mikahilenko et al., 1990) is still tricky. Also, to simulate reaction conditions properly, the catalyst should be used in its active form (Weller, 1992).

For the hydrogenation of unsaturated FAMEs, the kinetic rate expressions are often based on a Langmuir type of adsorption in combination with key surface intermediates. The underlying mechanisms expect the double carbon bond to adsorb at the active nickel sites, followed by hydrogen insertion steps at the surface (see Chapter 2 and 3). From hydrogenation experiments, the reactivity of double unsaturated FAMEs is some ten times higher, compared to monoenes, probably due to different adsorption strengths of the double carbon bonds to the nickel (Dutton, 1982; Coenen, 1986). The different reactivities between unsaturated bonds are usually expressed in their adsorption parameters, which appear then as fit parameters in the kinetic expressions (Gut et al., 1979; Chapter 3).

Independent adsorption isotherms on heterogeneous catalysts usually are experimentally measured by a mass-balance method (Parfitt and Rochester, 1983). Here, the amount adsorbed is calculated from the liquid concentration change. Advantages of such batch adsorption experiments, which have been used for more than a century, are their simplicity and straightforward interpretation. However, the major drawback is the occurrence of large detection inaccuracies (Everett, 1986), inherent to the relatively small concentration changes in the fluid, caused by adsorption on the surface. Therefore, mass-balance methods require a large surface area per unit mass, very high solids loads and special attention to the accuracy of the analytical techniques.

For liquid adsorption, tracer pulse experiments on packed columns usually is the most accurate experimental technique for determining adsorption parameters (Parfitt and Rochester, 1983). However, active Ni-based hydrogenation catalysts contain surface hydrogen and hence require pretreatment (activation, degassing) which is impossible in liquid tracer column experiments (Fouilloux, 1983).

In this study, we report adsorption phenomena of saturated and unsaturated FAMEs on both supported nickel as well as pure (Raney) nickel. Supported nickel was investigated in tracer pulse column experiments; the nickel was not re-activated, because of the impossibility of a proper degassing after packing. Adsorption of FAME

on pure nickel was performed in batch adsorption experiments, which allowed the use of Raney nickel in active form. To increase the experimental accuracy, very high catalyst loads, up to 60 w/w%, were applied in a specially developed autoclave.

5.2. Theory

5.2.1. Tracer Pulse Experiments. The column experiments were performed to investigate the interaction of the FAME with supported nickel catalyst. In chromatographic experiments performed with packed columns, any intraparticle adsorption of tracer is reflected in the average residence time of the tracer pulse (Ruthven, 1984). The Residence Time Distribution (RTD) curves of the tracers are normalised, applying the dimensionless residence time q , which is defined, in line with Chapter 4 (4.2.2)

$$q = \frac{tv}{L} \quad (5.1)$$

The adsorption parameters can be directly calculated from the dimensionless mean residence time q_m :

$$q_m = \int_0^{\infty} qE(q)dq = 1 + (1 - e_b)e_b^{-1}e_p(1 + K_s) \quad (5.2)$$

To use eq 5.2, the solute concentration should be sufficiently low to assume linear adsorption ($C_s = K_s C_l$, with C_s solid concentration [mol/m³] and C_l liquid concentration [mol/m³]). The linearity should be checked using the experimental data (Ruthven, 1984). Details of the chromatographic method can be found in Chapter 4. The catalyst used, the silica-supported-nickel catalyst Pricat 9933, was inactivated and therefore the hydrogenation reaction was absent.

5.2.2. Batch Adsorption Experiments. Raney-nickel could not be applied in packed columns, so batch adsorption experiments were carried out, in which activated Raney-nickel was used. The interaction of double bonds of FAME with pure, active, nickel surface was studied relative to the adsorption of fully saturated FAME. For this purpose, a mixture of FAMEs, which contains chemically almost equivalent molecules, apart from their degree of unsaturation, was defined as a pseudo-binary system of saturated and unsaturated molecules. We have used pseudo-bicomponent

mixtures only, which consist of monoene-saturated or polyunsaturated FAME mixtures only.

In batch adsorption experiments, preferential adsorption of one of the components at the surface is reflected by a relative change of (liquid) bulk concentrations after adding the solids to the fluid. By applying a mass balance over a slurry of catalyst in a binary mixture, Everett (1986) defined a surface excess parameter to couple the competition of the two components for surface sites to measurable parameters as concentrations and catalyst loads. The specific surface excess of e.g., monounsaturated FAME fractions, $n_M^{S(n)} / m$ [mol/kg_c], is then calculated from the experiments as

$$\frac{n_M^{S(n)}}{m} = \frac{n^0 \Delta x_{1,M}}{m} \quad (5.3)$$

For a binary mixture, $\Delta x_{1,M}$ follows directly from measuring the mole fraction of monounsaturated species in a liquid sample of the slurry. It should be mentioned that the theory only holds for a (pseudo) binary mixture, that is all monounsaturated or all double unsaturated versus saturated molecules, but it fails for a mixture of all kinds of unsaturated (mono and double) molecules. The superscript $S(n)$, denotes the excess of the monounsaturated FAME adsorbed at the surface relative to the amount adsorbed if no preferential adsorption of the monounsaturated FAME would occur, the latter referred to by n in $S(n)$.

The surface excess of the saturated components, $n_S^{S(n)}$, follows from Everett (1986)

$$n_M^{S(n)} = -n_S^{S(n)} = -n^0 (x_S^0 - x_S^{eq}) \quad (5.4)$$

with x_S^0 and x_S^{eq} initial and equilibrium mole fraction of the saturated components, respectively. The specific reduced surface excess of the unsaturated species is then calculated from (Everett, 1986):

with n^{\max} specific catalyst capacity for adsorption [mol/kg_c] and with the adsorption partition coefficient Ω defined by

$$\frac{n_M^{S(n)}}{m} = \frac{n^{\max} (\Omega - 1) x_S^{eq} x_M^{eq}}{\Omega x_M^{eq} + x_S^{eq}} \quad (5.5)$$

$$\Omega = \frac{x_{s,M}x_{l,S}}{x_{l,M}x_{s,S}} \quad (5.6)$$

with subscripts s and l denoting surface and liquid fractions, respectively. All parameters of eq 5.5 can be measured, apart from Ω , but the latter can be fitted by applying eq 5.5 on the experimental data.

In kinetic rate equations, the Langmuir adsorption coefficient is often applied instead of Ω . A typical Langmuir expression for FAME hydrogenation is (Gut et al., 1979; Chapter 2 and 3):

$$x_{s,M} = \frac{K_M x_{l,M}}{K_M x_{l,M} + K_S x_{l,S}} = \frac{\frac{K_M}{K_S} (x_{l,M} / x_{l,S})}{\frac{K_M}{K_S} (x_{l,M} / x_{l,S}) + 1} = \frac{\Omega (x_{l,M} / x_{l,S})}{\Omega (x_{l,M} / x_{l,S}) + 1} \quad (5.7)$$

with K_M and K_S Langmuir adsorption coefficients of the monounsaturated and saturated species, respectively (note that the subscript s in K_s denotes solid and S in K_S saturated components). The behavior of Ω with concentration becomes similar to K_s , the adsorption coefficient from tracer pulse experiments, if Ω is determined in the linear regime which is achieved for $\Omega(x_{l,M}/x_{l,S}) \ll 1$ and $x_{l,M} \ll x_{l,S}$ (see eq 5.6). Only with knowledge of the surface occupancy in m^2/kg_c , their numerical values can be mutually compared.

For hydrogenation catalysts, adsorption experiments under reaction conditions imply that the concentrations of the saturated and unsaturated species not only change due to adsorption effects, but also due to hydrogenation of unsaturated bonds. In the calculation of adsorption parameters, both effects have to be separated, which can be done as follows. Each mixture contains a fraction of saturated C16 methyl ester (P, methyl palmitate), which is chemically almost equivalent to the C18 methyl ester (S), but can be distinguished from it by gas chromatography. Because unsaturated C16 always was below the detection limit (<0.5%), the amount of methyl palmitate is not affected by hydrogenation and can be used as an internal standard for the amount of methyl stearate. The latter is formed due to hydrogenation of monounsaturated FAME. After completion of the hydrogenation, the mole fraction of saturated C18 corrected for hydrogenation, x_S^0 , is related to the measured mole fractions of methyl palmitate by

$$x_S^0 = x_S^{\text{eq}} \frac{x_P^0}{x_P^{\text{eq}}} \quad (5.8)$$

The recalculated initial mole fraction of monounsaturated FAME, calculated with x_S^0 , separates concentration changes due to adsorption from those due to reaction, which enables us to investigate adsorption phenomena under reaction conditions.

5.3. Experimental Section

5.3.1. Tracer Pulse Experiments. The tracer pulse experiments were performed in High Performance Liquid Chromatographic (HPLC) columns ($d_{\text{cl}} = 4.6 \times 10^{-3}$ m, $L = 0.10\text{--}0.15$ m) packed with a silica supported nickel catalyst (Pricat 9933, sample 1992, Unichema Emmerich). The columns showed an ideal plug flow behaviour (see Chapter 4). The values for e_b and e_p were determined as $e_b = 0.27$ and $e_p = 0.45$, respectively (Chapter 4). Experiments were carried out at $313 < T < 353$ K with either n-octane or a medium chain triglyceride oil (MCT oil, C10–C12 chains) as an eluent. The tracers used were methyl palmitate (P), n-hexadecane (HD) and trioleate (TO, a triglyceride with three oleic acids).

5.3.2. Batch Experiments. The Raney-nickel experiments were performed batch-wise at high catalyst loads (60 w/w%) which required the development of a special mixing cell (Figure 5.1), to prevent the occurrence of nonwetted zones. The novel mixing cell contains two separable parts entangling a sphere-shaped volume of 60 mL. A stirring device proved not to be efficient enough at these high catalyst loads, even when applying baffles, but tests proved that a shaking mechanism can perfectly mix the contents of the cell.

The following procedure was applied. Raney-Nickel (supplied by Alrich, catalytical surface of 10^5 m²/kg_c), activated by the manufacturer and stored in water, was brought into the cell, under a nitrogen atmosphere. Subsequently, the cell was purged with helium at $T = 353$ K and $P_r = 0.5$ mbar to remove residual water until the cell pressure remained stable when the vacuum pump was switched off. The liquid mixture was injected at a slightly elevated helium pressure at $T = 323$ K (T constant within 1 K) and equilibration was allowed for 18 h, after which four samples of 2 mL were subsequently pressed through an internal filter (see Figure 5.1) by means of

helium. The composition of the reactor samples was determined by gaschromatographic analysis (50 meter CP-Sil 88 column).

Several mixtures of fatty acid methyl esters were applied in the experimental series of batch adsorption experiments. Each mixture was defined as a pseudo-binary mixture: the total saturated versus unsaturated fraction (either mono- or double unsaturated) of FAMEs in order to investigate the adsorption behavior of double bonds, relative to fully saturated chains. Table 5.2 gives the fatty acid composition of the three mixtures. The monoene mixtures M1 and M2 are rich of methyl oleate, (O, commercial grade) and methyl erucate (C22:1, Er, specially prepared by Unilever Laboratories Vlaardingen) respectively. The diene mixture D contains mainly methyl linoleate, but also monounsaturated FAMEs. All mixtures also contained a small amount (about 7%) fully saturated methyl palmitate. An accurate GC analysis enabled the mutual comparison of adsorption phenomena of the different FAMEs.

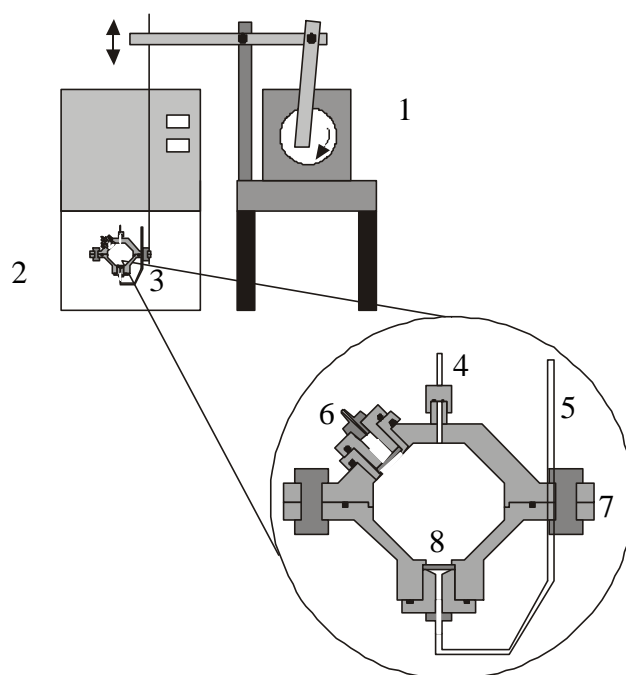


Figure 5.1. Novel mixing cell for mixing at high catalyst loads (60 w/w%). 1 = motor, 2 = thermostatted oil bath, 3 = autoclave, 4 = entrance for tracer, 5 = sample outlet, 6 = gas inlet, 7 = sealing of upper and lower half, 8 = filters.

Table 5.2. Composition of the Methyl Ester Mixtures used in the Adsorption Experiments and Characteristic Retention Time on Gas Chromatograph Diagram.

mixture ^a	saturated			unsaturated			rest
	C16:0 P	C18:0 S	C22:0 B	C18:1 O	C22:1 Er	C18:2 L	
compound ^b							
M1	6.72	13.7		77.5		1.68	0.40
M2			5.05		92.1		2.8
D	6.75	5.60		21.3		65.9	0.40
t_m (min) ^c	9.0	13.0	26.7	13.5–15.4	28.1–30.6	15.9–17.0	>8.5

^a M = monoene mixtures (1 and 2), D = diene mixture. ^b B, Er, etc., see Notation. ^c typical retention times on gaschromatograph, CP-Sil 88, 50 meter, internal diameter 0.25 mm, film thickness 0.20 μ m, 180 °C. Ranges of t_m are due to positional and geometrical isomers.

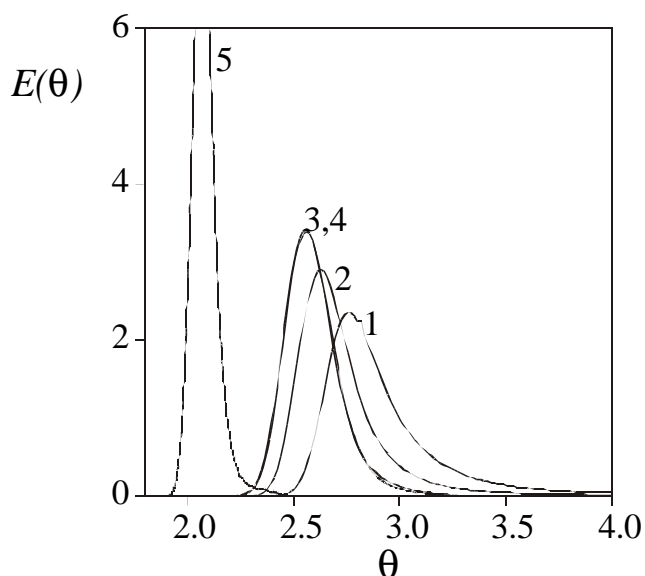


Figure 5.2. Residence time distribution curves for methyl palmitate at $T = 313$ K (1), 327 K (2), and 353 K (3,4); $C_{inj} = 0.8$ mol% (1,2,3), $C_{inj} = 4$ mol% (4). A typical RTD curve of *n*-hexadecane is also shown (curve 5, $T = 313$ K, $C_{inj} = 0.8$ mol%)

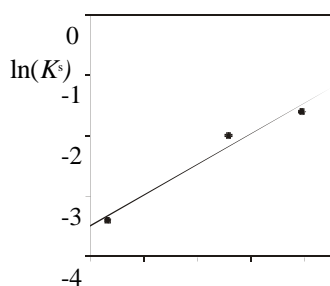


Figure 5.3. Van 't Hoff plot of K_s of methyl palmitate in *n*-octane, $C_{inj} = 0.8$ mol%

5.4. Results

5.4.1. Adsorption Data from Tracer Pulse Experiments.

Adsorption phenomena of FAME on supported nickel catalysts were observed for methyl palmitate with *n*-octane as an eluent. Figure 5.2 shows the RTD curves of methyl palmitate for various temperatures and initial concentrations. The curves of methyl palmitate are more symmetrical at elevated temperatures which is due to a decreasing adsorption strength. *n*-Hexadecane does not show any adsorption effects, indicating that the observed adsorption of methyl palmitate originates from adsorption of the methyl ester group. A typical response curve of *n*-hexadecane is included in Figure 5.2; the curves are remain for other temperatures. The injected concentration of methyl palmitate does not affect the RTD curve indicating that a linear adsorption constant can be applied. Figure 5.3 shows K_s , obtained with tracer pulse experiments, for methyl palmitate in *n*-octane in form of a Van 't Hoff plot. Although it should be

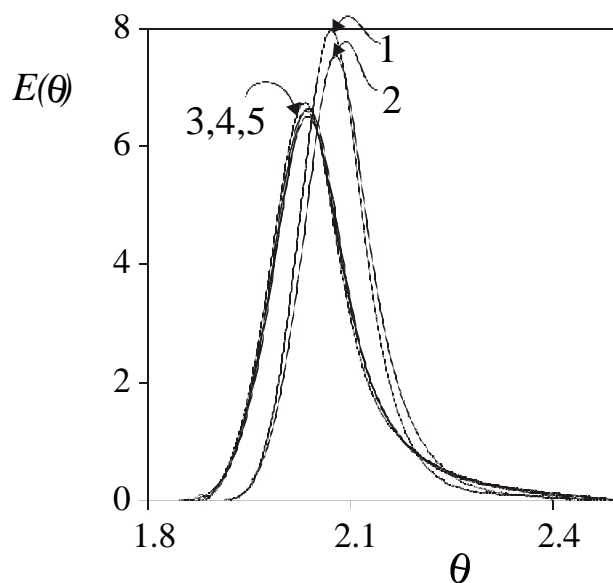


Figure 5.4. Residence time distribution curves for hexadecane (1), methyl palmitate (2), trioleate (3), and soy bean oil (4) in medium chain triacylglyceride, $T = 313$ K. For trioleate, the curve at $T = 300$ K is also shown (5).

mentioned that the applied temperature range is rather small, the resulting adsorption enthalpy $DH(K_s)$ of methyl palmitate on silica supported catalysts of -42 ± 5 kJ/mol appears to be reasonable. The value is between the adsorption enthalpies of FAME on

silica in benzene ($\Delta H(K_{ad}) = -35$ kJ/mol) and in carbon tetrachloride ($\Delta H(K_s) = -52$ kJ/mol), see Table 5.1.

The influence of the solvent is pronounced if *n*-octane is replaced by a medium chain triglyceride (MCT) as an eluent. With medium chain triglyceride, the RTD curves of methyl palmitate and *n*-hexadecane completely coincide (see Figure 5.4). Moreover, RTD curves of trioleate are insensitive to the column temperature (Figure 5.4), denoting negligible adsorption in medium chain triglyceride oil. The small difference between methyl palmitate/hexadecane and trioleate may stem from a different accessibility to the (crystalline) pores. Though methyl palmitate in *n*-octane adsorbs on supported nickel catalysts, it does not show any preferential adsorption with an oil as a solvent, indicating an interaction of the ester group with the surface.

5.4.2. Preliminary Tests for Batch Adsorption Experiments. For the batch adsorption experiments, which are far more sensitive to inaccuracies than tracer pulse experiments (Parfitt and Rochester, 1983), an elaborate sensitivity analysis of the experimental setup was carried out, as recommended by Everett (1986). The inaccuracy in the selectivity factor Ω appeared to originate for >99% from the inaccuracies in the mole fractions obtained from GC chromatography. Optimization of the injection and temperature programme minimized the standard deviation of the mole fractions to 0.005.

Parameter sensitivity calculations showed, that a catalyst load of >50% is needed to attain the experimentally determined $n_M^{S(n)}$ or $n_D^{S(n)}$ with confidence limits below 25%. The mixing efficiency of the cell was tested for several catalyst loads and mixing times. Within a few minutes, the catalyst appeared to be homogeneously mixed with the fluid, which could be observed by pouring the reactor contents on to a glass plate.

Activation of the Raney nickel catalyst, which was preactivated by the manufacturer, required the removal of surface bonded hydrogen before the liquid mixture was added. Therefore the cell was degassed by applying vacuum at the maximum allowable reactor temperature of 353 K. However, at this temperature part of the hydrogen may remain at the catalyst surface (Fouilloux, 1983; Babenkova et al., 1994). If so, some hydrogenation still may take place. Only at $T > 600$ K (Fouilloux, 1983; Babenkova et al., 1994) all hydrogen can be removed. Applying such high temperatures is not recommended because, apart from the experimental difficulties, the catalyst surface may be subject to sintering (Fouilloux, 1983; Kinza et al., 1985; Mikhailenko et al., 1993). A possible advantage of removing only a part of the surface

bonded hydrogen is that the adsorption of FAMEs can be studied under circumstances which are as close as possible to reaction conditions.

The effect of hydrogenation on the adsorption measurements was established by varying the time of degassing and stabilisation. It appeared that after 18 h under 0.5 mbar, the hydrogenation of FAMEs by surface hydrogen was completed for about 90%, see Figure 5.5. At this point, the hydrogenation rate is sufficiently reduced to keep changes in the liquid concentrations negligible within the sampling time (<2 minutes). Then, 0.6 mol/kg_c is hydrogenated (see Figure 5.5), which is about half of the initially 1.2 mol/kg_c (Fouilloux, 1983) of hydrogen. This way, FAME adsorption on an hydrogen-rich surface is measured. In some experiments, the equilibration time was varied between 1.5 and 88 h. It appeared that the equilibration time had no influence on the amount adsorbed. Therefore, we choose the recommended 18 h of equilibration in all experiments (Everett, 1986).

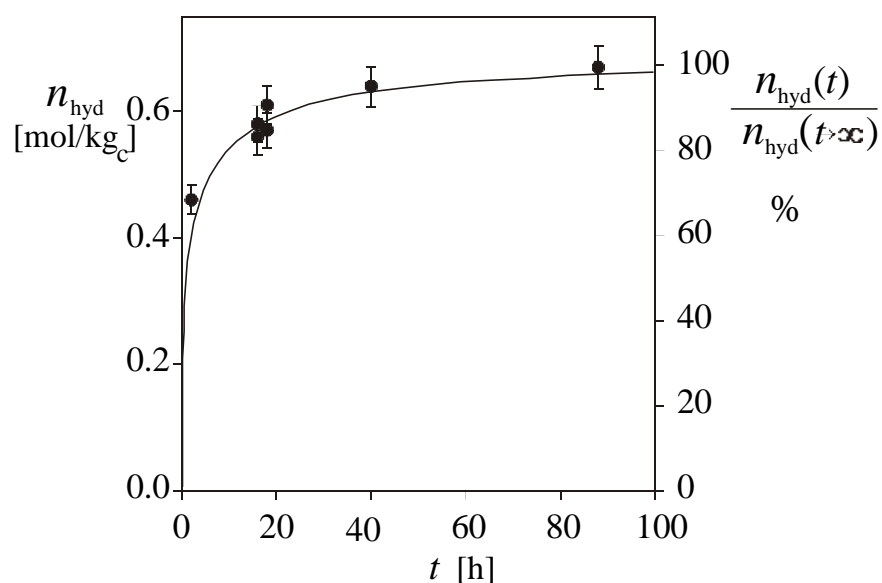


Figure 5.5. Hydrogenated unsaturated fatty acid per kg catalyst with 95% confidence interval, as a function of the stabilisation period at $T = 323$ K.

5.4.3. Batch Adsorption Experiments with Monounsaturated Mixtures. Figure 5.6 summarizes the specific surface excess of the adsorption experiments on Raney-nickel in terms of the total fraction of monounsaturated species. The solid line, calculated from eq 5.5, is a close fit of the data points, with optimized values for Ω and n^{\max} , which are >100 and $0.08 \pm 0.02 \text{ mol/kg}_c$, respectively. The value of $\Omega > 100$ in fact implies a very strong adsorption of unsaturated relative to saturated species. For comparison, $\Omega = 10$ is also drawn in Figure 5.6. From $n^{\max}=0.08 \text{ mol/kg}_c$ and a catalyst surface of $10^5 \text{ m}^2/\text{kg}_c$ for Raney-nickel (data from manufacturer), an occupied surface per molecule of 2.2 nm^2 can be calculated. This value indicate that the molecules do not lie flat to the surface, otherwise the occupied surface would be 8–9 times larger (Mills and Hockey, 1975).

The value of Ω can be related to adsorption parameters obtained from

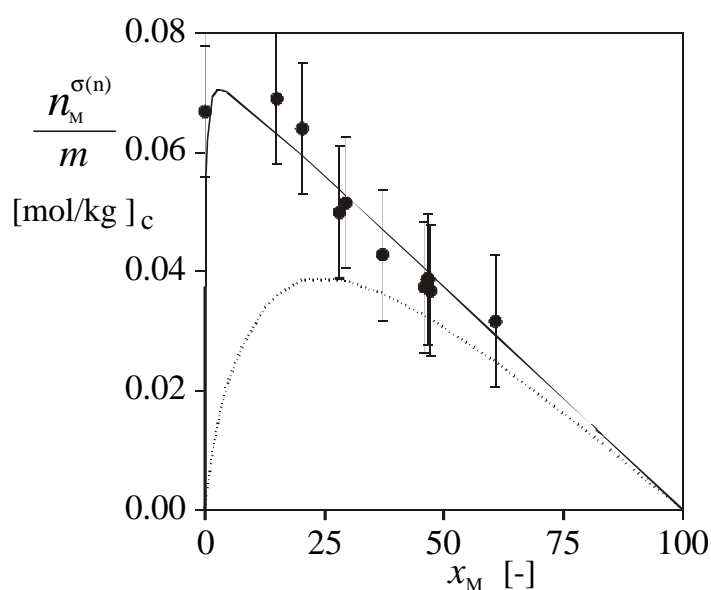


Figure 5.6. Specific reduced surface excess for monounsaturated FAMES mixtures ($T = 323 \text{ K}$) on Raney-nickel. Solid line is a fit of the experimental points (with 95% confidence interval), calculated with eq 5.5 and $\Omega > 100$ and $n^{\max} = 0.08 \text{ mol/kg}_c$. As an example $\Omega = 10$ is also drawn (dotted line). For the compositions of the initial mixtures, see Table 5.2, M1 and M2.

hydrogenation data on silica-supported-nickel. Gut et al. (1979) found for K_M/K_S (equal to Ω , see eq 5.7), which is the Langmuir adsorption constant of monounsaturated C18 FAME (K_M), relative to saturated FAME, methyl stearate (K_S), $4.4 < K_M/K_S < 0.9$ for $413 < T < 513 \text{ K}$. Also, in Chapter 2 was found $K_M/K_S = 3$ for $333 < T < 413 \text{ K}$. So, the data of Gut et al. (1979) and Chapter 2 indicate a preferential adsorption of monounsaturated components, relative to saturated ones. The much

lower value of Ω measured on supported nickel, compared with Ω obtained for pure nickel, may stem from additional adsorption of the methyl ester group on the catalyst support.

5.4.4. Batch Adsorption Experiments with Double unsaturated Mixtures. In the calculation of adsorption of diene (D), relative to monoene (M), the consecutive reaction, $D \rightarrow M \rightarrow S$, should be incorporated, to distinguish between the hydrogenation of D and M. The change in concentration of D and M cannot be separated in an adsorption and a hydrogenation part, without knowledge of the exact values of the hydrogenation rate of $D \rightarrow M$ and $M \rightarrow S$. However, calculations showed that very small variations in the hydrogenation parameters (within 3%) largely change the calculated surface fractions (>50%). Literature data of kinetic parameters of these reactions are too inaccurate and too catalyst specific to calculate the amount of diene hydrogenated to monoene. Therefore, because the D(iene) mixture (see Table 5.2) inevitably also contains monounsaturated components, the concentration changes in the batch adsorption experiments of monoenes and dienes cannot be accurately separated the contributions of adsorption and hydrogenation. Consequently, quantitative data on diene adsorption could not be gathered.

However, the formation of specific reaction products enabled us to perform a qualitative evaluation of adsorption of dienes and monoenes. Apart from hydrogenation and adsorption, we also observed chain shortening and double bond isomerization. The chain shortening from C18 to C17 to C16 and so on appeared to take place on a low but significant level. Table 5.3 summarizes the calculated ratio of C17 to C18 for different temperatures and times. These observations are in line with literature: Machiels and Anderson (1979) reported that nickel catalysts preferentially attack terminal carbon-carbon bonds and successive demethylation is found for a number of alkanes, ranging from pentane to decane. Double bond isomerization, both positionally and geometrically, is well known (see e.g., Van der Plank, 1972). Applying the diene mixture, which mainly contains the conjugatable methyl linoleate (9,12, *cis, cis*), we also observed the formation of

Table 5.3. Chain Shortening of C18 or Demethylation as $f(T,t)^a$

<i>T</i> , K	<i>t</i> , h	C17/C18 mol%
323	18	1.5
353	6	2.0
353	27	2.3
373	19	3.0

^a values are corrected for initial concentrations

conjugated FAMEs. Their products appeared to be useful in interpreting adsorption phenomena.

Table 5.4. Chain shortening and conjugation in adsorption experiments with monoene and diene mixtures. Composition of M1, M2 and D, see Table 5.2.

exp	mixture	T (K)	t^a , h	C17/ C18 ^b , %	conj. ^c %	remarks
monoene mixture						
1	M1	323	20	1.5		
2	M1+M2	323	15	1.3		Er similar to O ^d
diene mixture						
3	D	323	16		6.3	
4	D	323	18	1.8		L completely hydrogenated to O ^d
5	D+M2	323	18		6.6	no isomers of Er ^d

^a time (h), calculated from injection of FAME mixture. ^b ratio of C17 to C18 chain in GC analysis.

^cconj.: ratio of conjugated species to linoleate (and isomers) in %. ^d Er = methyl erucate (C22:1); O = methyl oleate (C18:1); L = methyl linoleate (C18:2).

In a series of experiments, we repeatedly observed that conjugated species were only detected if dienes were present, while demethylation only occurred in the absence of dienes, for chemically unknown reasons. The key experiments are summarized in Table 5.4. In experiment 2, some methyl erucate was added to the oleate mixture, which delivered similar isomer formation. In the diene adsorption experiments, conjugated dienes were significantly formed (about 6–7%), except in experiment 4, where all dienes were hydrogenated to monoenes and demethylation occurs. From experiment 5 we may conclude that dienes preferentially adsorb above monoenes, because in a mixture of D and M2, the monoene methyl erucate (C22:1) did not show any isomers in the liquid. This result is in line with Chapter 3 where, from fitting rate equations to hydrogenation data, a preferential adsorption of diene, relative to monoene was found too.

5.5. Conclusions

For studying adsorption phenomena of saturated and unsaturated fatty acid methyl esters, a novel type of mixing cell was developed, which could mix slurries with solids loads as high as 60 w/w%. Also experiments were carried out with tracer pulse experiments.

In chromatographic experiments with *n*-octane as an eluent, methyl palmitate adsorbed on the deactivated nickel-silica surface, $DH(K_s) = -42 \pm 5$ kJ/mol ($313 < T < 353$ K), while adsorption of *n*-hexadecane was absent, which shows the interaction of the methyl ester group with the silica surface. With medium chain triglyceride oil as an eluent, the adsorption phenomena of methyl palmitate and trioleate disappeared.

To investigate double bond adsorption at reaction conditions, activated Raney nickel catalyst was used in batch adsorption experiments. At $T = 353$ K, the adsorbed hydrogen on the Raney-nickel catalyst could only partly be removed by applying vacuum. As a result, some hydrogenation of unsaturated FAMES occurred in the adsorption experiments. In this way, the adsorption experiments closely resembled reaction conditions.

The batch adsorption experiments showed that monounsaturated FAMES preferentially adsorbs to saturated FAMES and occupy an adsorption surface of 2.2 nm² per molecule. Also chain shortening of C18 to C17 and further (demethylation), was observed as well as the formation of conjugated species of the conjugatable double unsaturated methyl linoleate. Both effects could be used to prove qualitatively that methyl linoleate preferentially adsorbs to monounsaturated FAMES on the nickel surface.