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Fatty Acid Hydrogenation

Unprecedented Shape Selectivity in Hydrogenation of Triacylglycerol Molecules with Pt/ZSM-5 Zeolite**

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Vegetable oils are made up of triacylglycerol molecule mixtures, which comprise three fatty acids esterified to a glycerol backbone. The fatty acids can differ in chain length, number, and double-bond configuration. Common vegetable oils contain fatty acid chains with 16 to 20 carbon atoms and 0 to 3 double bonds, all of which are in a *cis* configuration (Table 1).[1] Fatty acid chains are located at the central (*sn*-2) or outer (*sn*-1,3) positions on the glycerol backbone. Thus SOS refers to oleate at the *sn-2* and stearate at the *sn*-1,3 positions.

Table 1: Description and notation of common C_{16}/C_{18} fatty acid chains in triacylglycerols.

Chain name	Double bonds[a]			Notation[b]
	n[a]	position	conf.[b]	
palmitate	0	–	–	C16:0
stearate	0	–	–	C18:0
oleate	1	9	*cis*	C18:1 *c*9
elaidate	1	9	*trans*	C18:1 *t*9
linoleate	2	9,12	*cis*	C18:2 *c*9*c*12
linolenate	3	9,12,15	*cis*	C18:2 *c*9*c*12*c*15

[a] *n* = number, conf. = configuration. [b] *c* = cis, *t* = trans.

Partial hydrogenation of highly unsaturated vegetable oils with a nickel-based catalyst is used in the food industry to stabilize the oils against autoxidation.[2] Unfortunately, a significant degree of *cis*/*trans* isomerization simultaneously leads to formation of *trans* fatty acid chains, such as E on some of the triacylglycerols, which leads to a serious risk of cardiovascular disease.[3] Many unsuccessful efforts have also been published concerning the double-bond reduction of vegetable oils yielding semi-solid fat products with specific melting properties for use as shortenings and bakery fats with low levels of *trans* fatty acids.[4]

We recently reported the preparation of a shape-selective Pt/NaZSM-5 catalyst, which enables the bent *cis* chain in methyl oleate (MO) and the linear *trans* chain in methyl elaidate (ME) to be discriminated during room-temperature adsorption and hydrogenation.[5] Herein, unprecedented shape selectivity on zeolites with MFI topology during adsorption and on Pt/ZSM-5 during hydrogenation of model triacylglycerols was demonstrated. Applied to vegetable oils, this should allow the conversion of unsaturated oils into autoxidatively stable products, which are useful as a basis for dressing oils, shortenings, or bakery fats devoid of *trans* fatty acid chains.

Results from room-temperature sorption experiments of ME, MO, EEE (trielaidate), and OOO (trioleate) on NaZSM-5/78 and reference γ-alumina are given in Table 2. Adsorption equilibrium constants *K* of ME and MO on γ-alumina show hardly any difference for the respective geometric isomers. Compared to the *trans* isomers, the sorption is even slightly in favor of the *cis* isomer, which is attributed to its better access to the wall of a non-constrained pore. With MFI zeolite, discrimination among *cis* and *trans* chains is found for methyl esters as well as for triacylglycerols, with sorption being in favor of the slimmer *trans* fatty acid chains. The strongly reduced values of the sorption constants for triacylglycerols compared to methyl esters point to the inaccessibility of the intracrystalline zeolite space, with sorption being limited to pore mouth penetration of only one of the chains of the triacylglycerol.

Table 2: Room-temperature adsorption equilibrium constants *K* of geometrically different mono-unsaturated methyl esters and triacylglycerols.[a]

Adsorbent	K_{ME}	K_{MO}	K_{ME}/K_{MO}	K_{EEE}	K_{OOO}	K_{EEE}/K_{OOO}
Na-ZSM-5	6.09	5.08	1.20	1.14	1.01	1.13
γ-alumina	1.01	1.00	1.01	0.61	0.67	0.91

[a] Mono-unsaturated methyl esters: ME = methyl elaidate, MO = methyl oleate; triacylglycerols: EEE = trielaidate, OOO = trioleate.

As a measure of the hydrogenation rate, the first-order rate constant *k* was divided by the chromatographically determined adsorption equilibrium constant *K*. Indeed, under conditions of substrate dilution and limited hydrogen solubility, a bimolecular Langmuir–Hinshelwood rate equation transforms into an equation that is first-order in both reactants. With the Pt/alumina catalyst (Table 3), the hydro-

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Table 3: Hydrogenation rate k/K of mono-unsaturated fatty acid chains of methyl esters and triacylglycerols.[a]

Catalyst	k/K ME	MO	EEE	OOO
1Pt/ZSM-5/78[b]	0.071	0.067	0.85	0.57
2Pt/γ-alumina[c]	2.60	3.57	2.12	2.70

[a] 2.0 wt% substrate in *n*-octane at 100°C and 6 MPa of hydrogen; k [h^{-1}], the first-order rate constant and K, the adsorption equilibrium constant were determined chromatographically under the same conditions. [b] Catalyst/substrate weight ratio 0.1 wt%. [c] 0.01 wt%.

genation rate of *cis* chains is favored, which is attributed to a better contact between the platinum surface and the double bond, and the values for the respective methyl esters and the triacylglycerols are comparable. With the zeolite-based catalyst, hydrogenation of *trans*-configured chains is faster in both cases. The higher rates for hydrogenation of triester compared to monoester molecules is again in line with pore mouth hydrogenation on occluded platinum particles compared to reaction inside zeolite pores. TEM images of the Pt/ZSM-5 catalyst (Figure 1) indeed show homogeneously distributed platinum clusters inside the crystals with a narrow particle size distribution and a mean platinum cluster size of (1.7 ± 0.8) nm.

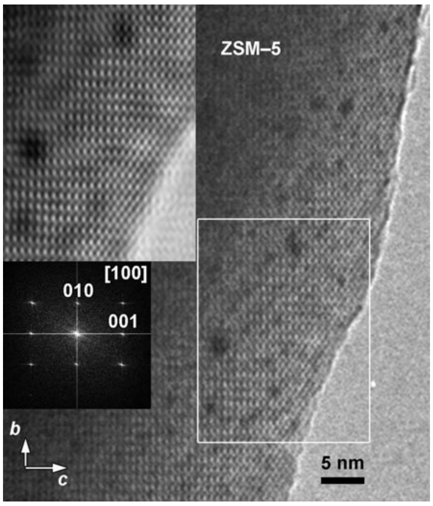

Figure 1. TEM image of 0.5 wt% Pt in ZSM-5. The ZSM-5 crystal is imaged along the [010] zone axis orientation (shown by FFT pattern; lower left). The Pt nanoparticles (dark contrast spots) are approximately 1–3 nm in diameter. Inset (top left): Bragg-filtered image of the region indicated by the white rectangle. The pore arrangement of ZSM-5 appears and the Pt nanoparticles (dark contrast) are visible.

Table 4: Hydrogenation rate k/K of mono-unsaturated fatty acid chains in triacylglycerols.[a]

Catalyst	k/K PEP	PPE	POP	PPO
1Pt/ZSM-5/78[b]	1.69	0.87	1.04	0.60
2Pt/γ-alumina[c]	0.96	0.86	1.32	1.19

[a] For conditions, see Table 3. [b] 0.6 wt% in octane; 0.05 wt% catalyst to substrate. [c] 0.01 wt% in octane; 0.001 wt% catalyst to substrate.

Hydrogenation of triacylglycerols with an unsaturated chain at a different position on the glycerol backbone, namely POP, PPO, and PEP, PPE, reveals the existence of position selective preferences, indicating that double bonds in fatty acid chains at position *sn*-1/3 or *sn*-2 react differently. Hydrogenation with Pt/alumina is faster for the O-containing triacylglycerols POP and PPO compared to corresponding E-containing PEP and PPE (Table 4). This result confirms the data obtained with other substrates (Table 3). Interestingly, with the microporous zeolite catalyst the differences are opposite, E-containing triacylglycerols being more reactive than O-containing forms, which is in agreement with the data in Table 3. Moreover, for both chain configurations (E and O), it is striking that the chain at *sn*-2 is more reactive with the zeolite catalyst than at positions *sn*-1,3, and the effect is much more pronounced for E chains.

Studies of the conformation of triacylglycerols in the solid state are numerous.[6] A recent modeling analysis of PPP and OOO shows that in the crystalline phase, conformations show a decreasing concentration in the following order: tuning fork (A), chair (B), and trident (C). In the fluid phase, the random conformation (D) of the triglycerides dominates over specific configurations.[7] It is therefore expected that the random conformation of POP, PPO, PEP, and PPE in solution will be dominant. However, the preferred hydrogenation of E and of O at position *sn*-2 (Table 4) points to a specific adsorption and reaction mode of triacylglycerols on the surface of ZSM-5 crystals according to the tuning fork conformation, probably with the central fatty acid chain protruding in pore apertures, thus allowing contact of double bonds on this chain with platinum metal particles in pore mouths.[8] As the triacylglycerol molecules are unable to enter the pores, chains at positions *sn*-1,3 are expected to be adsorbed in an energetically favorable configuration on the external surface of the zeolite crystals.

Regioselective analysis of products after partial hydrogenation of trilinoleate confirms the preferred reduction at the central linoleate (L) chain with Pt/ZSM-5, pointing to preferred adsorption of triacylglycerols at the crystal surface in the tuning fork (A) rather than the chair (B) or random (D) conformation (Figure 2, Figure 3). This regioselective hydrogenation will lead to reduced SSS levels in hardened fats and thus to more desirable physical properties.[9] With the alumina-based catalyst, such positional discrimination is absent.

Autoxidative stabilization of vegetable oils by catalytic hydrogenation with hydrogen requires selective removal of triene chains[10] and for dietary reasons retention of other *cis* unsaturates.[11] Therefore, selective stepwise reduction of the double bonds on a polyene chain should occur at a decreasing rate. Platinum is known to be lack such properties,[12] as confirmed in the distribution of chains upon partial reduction of LLL with platinum/alumina catalyst (Table 5). Surprisingly, platinum in the micropores of ZSM-5 zeolite shows this preferred stepwise reduction, as shown by much enhanced

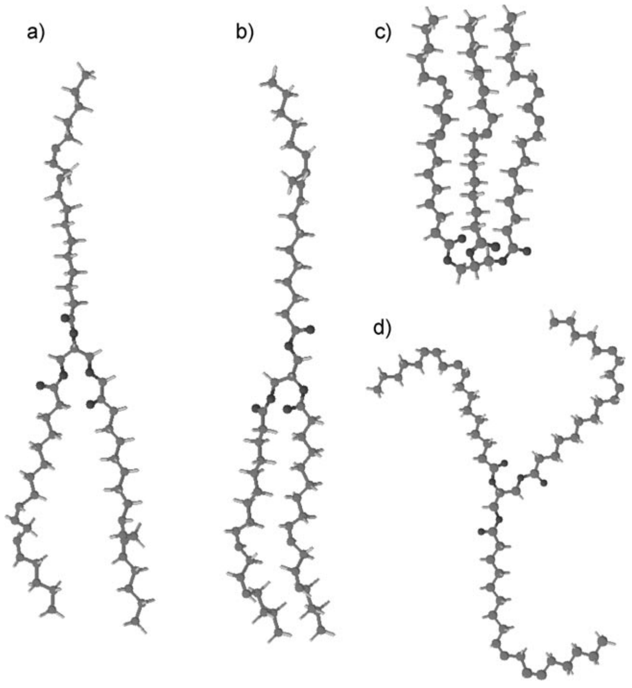

Figure 2. Possible conformations of triacylglycerols: a) tuning fork, b) chair, c) trident, d) random.

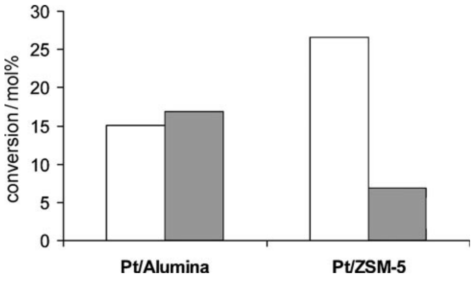

Figure 3. Conversion of double bonds at the central (*sn*-2; white bars) and outer positions (*sn*-1/3; gray bars) of partially hydrogenated trilinoleate using Pt/alumina and Pt/ZSM-5.

Table 5: Distribution of hydrogenation products from trilinoleate at 24% conversion.[a]

Catalyst	C18:0	C18:1*c*9	C18:1*c*12	C18:1*t*
0.5Pt/ZSM-5/138	39.0	27.6	28.0	6.4
0.5Pt/γ-alumina	87.2	7.7	5.1	0.0

[a] 2.0 wt% in *n*-octane at 65 °C and 6 MPa of hydrogen.

formation of monoene chains and reduction of saturated chains (Table 5). The latter behavior should be correlated with the tuning fork sorption mode of triacylglycerols on zeolite combined with enhanced affinity of more polar chains (trienes > dienes > monoenes) for the polar pore mouths of MFI. It can also be seen in Table 5 that discrimination among the *cis* monoenes (9 and 12) does not occur.

In conclusion, it is clear that shape-selective hydrogenation of model triacylglycerols on a Pt/ZSM-5 catalyst prefers *trans* over *cis* hydrogenation of the fatty acid chains. Moreover, the chain on the central position of the glycerol backbone is preferably reduced, and indicates pore-mouth adsorption in the tuning fork conformation. This adsorption mode allows discrimination among central chains with different polarities. The overall hydrogenation specificities will allow the synthesis of more healthy fats/oils (low in *trans*, high in oleic) with desirable physical properties (low SSS) from real feedstocks. Experiments are planned to confirm this experimentally.

Experimental Section

Model compounds were obtained from Larodan and Sigma Aldrich. Hydrogenation was carried out with hydrogen in a stirred batch reactor. Further information about the experiments is given in the Supporting Information.

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