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Selectivity in sorption and hydrogenation of methyl oleate and elaidate on MFI zeolites

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ABSTRACT

Different zeolites were tested for selective removal of methyl elaidate (*trans* isomer) from an equimolar mixture with methyl oleate (*cis* isomer). Sorption experiments of the geometric isomers show that only ZSM-5 samples with reduced Al content in the framework are able to discriminate among the bent *cis* and the linear *trans* fatty acid methyl esters. Hydrogenation experiments of equimolar methyl oleate and elaidate mixtures at low temperature (65 °C) and high hydrogen pressure (6.0 MPa), using Pt catalysts, confirm this result. Only with a Pt/Na–ZSM-5 catalyst outspoken selectivity for the hydrogenation of the *trans* isomer is obtained. In order to prepare a selective Pt/ZSM-5 catalyst, the influence of Pt addition (impregnation, ion-exchange and competitive ion-exchange) and Pt activation (different calcination and reduction temperatures) on the Pt-distribution and Pt particle size was investigated using SEM, bright-field and HR TEM, EDX, electron tomography, CO-chemisorption, XPS, XRD, and UV–vis measurements. The best result in terms of hydrogenation activity and selectivity is obtained with a Pt/ZSM-5 catalyst, which is prepared via competitive ion-exchange, followed by slow calcination up to 350 °C under high O_2 flow and a reduction up to 500 °C under H_2. This preparation method leads to a Pt/ZSM-5 catalyst with the best Pt distribution and the smallest Pt clusters occluded in the zeolite structure. Finally, the influence of zeolite crystal size, morphology, and elemental composition of ZSM-5 on hydrogenation activity and selectivity was investigated in detail.

1. Introduction

Vegetable oils, like soybean oil, consist of triglyceride molecules, composed of three fatty acids attached to a glycerol backbone [1]. Whereas in naturally occurring molecules, the fatty acids have an even number of C atoms, they can occur with different chain lengths and different numbers of double bonds. The most common fatty acid chains in vegetable oils consist of 18 carbon atoms, containing between 0 and 3 double bonds, *viz.* stearic (C18:0), oleic (*c*C18:1), linoleic (*c*C18:2), and linolenic acid (*c*C18:3), the geometric configuration of natural fatty acid residues in triglycerides being *cis* w.r.t. the double bonds.

Catalytic hydrogenation of vegetable oils is a well-known process in food industry to make the oil more resistant against air autoxidation. For physiological reasons, it is desirable to hydrogenate *c*C18:3 chains, unstable against autoxidation, into *c*C18:2 and *c*C18:1, with limited formation of C18:0. Commercial hydrogenation is often conducted with a Ni catalyst between 180 and 200 °C using hydrogen pressures in the range of 50–250 kPa [2], resulting not only in saturation of double bonds, but also in formation of significant amounts of positional and geometric isomers. The presence of *trans* isomers in the fatty acid chains of edible oils, *viz.* elaidate (*t*C18:1), are legally restricted for dietary reasons [3–5]. Main efforts from industry to obtain products low in *trans* include: (1) changes of the hydrogenation parameters [2,6], (2) use of noble metal catalysts containing Pt and Pd [7,8], (3) use of catalytic transfer [9,10], electrocatalytic hydrogenation [11–13] and hydrogenation in supercritical conditions [14–17], (4) use of alternative processes and feeds, including chemical [18,19] and enzymatic interesterification [20], fractionation [21], and (5) use of naturally stable oils low in linolenic acid [22,23].

One aim of the present research is to investigate the fundamental basis for selective removal of *trans* isomers from a hydrogenated/stabilized oil sample via sorptive and size exclusion

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phenomena. This investigation was done at the level of the methyl esters of the fatty acids which in practice are obtained via a simple base catalyzed transesterification of triglycerides with methanol. Zeolites are obvious candidates for such studies. Possibly, the zeolite pore structure will allow to discriminate among the linear *trans* and the bent *cis* chain of the fatty acid methyl ester, *viz.* methyl elaidate (ME, C18:1 *trans*-9) and methyl oleate (MO, C18:1 *cis*-9), respectively.

Second, selectivity in the co-hydrogenation of MO and ME was examined on platinum loaded on zeolites. Pt was chosen as the active metal because of its low double bond isomerization characteristics [24,25]. Ideally, only *trans*-methyl esters of fatty acids should enter the pores of the zeolite and be hydrogenated selectively on the intracrystalline metal phase. The *cis* isomers, with a larger diameter, would be excluded from the pores and thus from the hydrogenation function.

Work is in progress investigating the possibility of extrapolating the concepts from fatty acid methyl esters to triglycerides.

2. Experimental

2.1. Materials

The origin and properties of zeolite supports used, *viz.* commercial and home-made zeolites, are shown in Table 1. Zeolites with different topology, pore size and pore architecture, crystal size, and Si/Al-ratio was selected. γ-Alumina was from Aldrich (type 507C) with a specific surface area of 200 m^2/g. Chemicals used for zeolite synthesis were from Acros. $Pt(NH_3)_4Cl_2$ was from Strem Chem. Methyl oleate and methyl elaidate were from Sigma–Aldrich with a purity of more than 99%.

2.2. Synthesis of ZSM-5

Synthesis of ZSM-5 zeolites according to a published procedure [26] was done with colloidal SiO_2 (LUDOX® AS-40, 40 wt.% suspension in water) as Si-source, $Al(NO_3)_3 \cdot 9H_2O$ as Al-source, tetrapropylammonium (TPA) bromide as templating agent and 1-hexanol/water mixtures as solvent. To a first solution with the following molar composition:

$$(SiO_2)_{1.00}(TPA)_{0.07}(hexanol)_{2.99}(H_2O)_{16.00}$$

a second solution containing various amounts of $Al(NO_3)_3 \cdot 9H_2O$ and NaOH in water was added under stirring so as to obtain a solution with the following molar composition:

$$(Na_2O)_x(AlO_2)_y(SiO_2)_{1.00}(TPA)_{0.07}(hexanol)_{2.99}(H_2O)_{32.00}$$

The values for x and y can be extracted from Table 2.

The solution was then placed in a Teflon autoclave and heated in a Milestone Microsynth Microwave oven for 17 h at 170 °C. Table 2 gives an overview of the compositions of the synthesis solutions for the different ZSM-5 samples. After synthesis the crystals were washed three times with distilled water and calcined in a muffle furnace for 24 h at 550 °C in order to remove occluded organics. XRD analysis confirmed that all samples were 100% crystalline w.r.t. a standard ZSM-5 sample. A combination of yield determination of the synthesis with chemical analysis of the obtained powder indicated that the synthesis efficiency both on Si and Al basis was always around 100 ± 5%. Sample notation involves the zeolite name, preceded by the name of the charge compensating cation and followed by the Si/Al framework ratio, *viz.* Na–ZSM-5(138). A capital C in the sample notation stands for a commercial sample, while MW refers to a lab synthesis in a microwave oven, as described previously.

2.3. Synthesis of Pt catalysts

Pt was introduced in the different supports via three different techniques, *viz.* incipient wetness impregnation (IWI), ion-exchange (IE) or competitive ion-exchange (CIE).

For IWI, an amount of a 0.0427 M aqueous solution of $Pt(NH_3)_4Cl_2$ with volume equal to the total water sorption capacity of a *vacuo*-dried zeolite (0.5 mL/g) was added dropwise to the dry zeolite powder. The catalyst powder was then dried overnight at 110 °C.

IE was done under stirring for 48 h of a zeolite in water slurry, containing the required amount of Pt-precursor in a 200-mL aqueous solution (usually 0.128 mM) per gram of dry zeolite. Prior to metal loading, calcined zeolites were brought in the Na-form via two successive room temperature ion-exchange steps lasting for 16 h. Two hundred milliliters of an aqueous 1 M NaCl solution per gram of dry zeolite was used. After each exchange, the filtration residue is washed three times with distilled water and dried at 100 °C. To achieve a complete Na ion exchange, prior to ion-exchange calcined as-synthesized samples were dropped into aqueous ammonia solutions of pH 10, followed by thorough washing with bidistilled water till neutral pH in the washing waters.

During CIE, the Pt ion-exchange was done in presence of Na ions (NaCl), using a Na/Pt atomic ratio of 25.

The metal content of the exchange solution after reaction was determined by Inductively Coupled Plasma Atomic Absorbance

Table 1
Origin and characteristics of used zeolite supports.

Entry	Zeolite type	Topology	Pore size[a]/dimensionality	Si/Al	Crystal size (μm)	Origin
1	Y	FAU	12MR/3D	2.7	2–3	Zeolyst
2	USY	FAU	12MR/3D	40.0	0.3–0.5	Zeolyst
3	Beta	BEA	12MR/3D	9.9	0.2–0.4	Zeocat
4	Mordenite	MOR	12MR/1D	6.2	1–2	Zeocat
5	Mordenite	MOR	12MR/1D	11.0	1–2	Zeocat
6	Mordenite	MOR	12MR/1D	100.0	1–2	Zeocat
7	L	LTL	12MR/1D	3.9	1	Zeocat
8[c]	ZSM-5	MFI	10MR/2D	40.0	0.3–1.0	Zeolyst
9	ZSM-5	MFI	10MR/2D	78.0	0.5–2.0	Zeolyst
10[d]	ZSM-5	MFI	10MR/2D	138.0	0.4–4.0	Zeolyst
11[b]	MCM-22	MWW	10MR/3D	15.0	2.0–3.0	[48]
12[b]	ZSM-22	TON	10MR/1D	51.0	2.0–3.0	[49]
13[b]	ZK-5	KFI	8MR/3D	2.3	0.4–0.8	[50]

[a] *x*-Membered ring (number of O- or T-atoms atoms circumscribing the main channels).

[b] Home-made according to published procedures.

[c] Sample Na–ZSM-5(C40) in Table 9.

[d] Sample Na–ZSM-5(C138) in Table 9.