

Selective Hydrogenation of Sunflower Seed Oil in a Three-Phase Catalytic Membrane Reactor

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ABSTRACT: Continuous hydrogenation of sunflower seed oil has been carried out in a novel three-phase catalytic membrane hydrogenation reactor. The membrane reactor consisted of a membrane impregnated with Pd as the active catalyst, which provided a catalytic interface between the gas phase (H_2) and the oil. Hydrogenations were carried out at different pressures, temperatures, and selectivities, and the formation of *trans* isomers was monitored during the hydrogenation runs. For the three-phase catalytic membrane reactor, interfacial transport resistances and intraparticle diffusion limitations did not influence the hydrogenation reaction. Hydrogenation runs under kinetically controlled conditions showed that oleic and elaidic acid were not hydrogenated in the presence of linoleic acid. Initial formation of stearic acid was caused by direct conversion of linoleic acid into stearic acid by a shunt reaction. Furthermore, high selectivities led to high *trans* levels, which is in accordance with the many published data on hydrogenation of vegetable oils in slurry reactors. Finally, the catalytic membrane showed severe catalyst deactivation. Only partial recovery of the catalyst activity was possible.

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Hydrogenation of vegetable oils to improve oxidative stability and change melting point has been an industrial process since the beginning of the twentieth century. The hydrogenation reaction is usually carried out over a nickel catalyst suspended in the liquid oil, and H_2 is supplied from the gas phase. When the vegetable oil contains polyunsaturated fatty acids, the selectivity of the hydrogenation process becomes an important parameter. Ideally, the polyunsaturated fatty acids should be hydrogenated first to monounsaturated fatty acids, which are then consecutively saturated. However, the selectivity of this reaction is limited. Selectivity increases with increasing temperature and decreasing hydrogen pressure. [For more detailed information, several literature reviews are available (1–3).]

The hydrogenation reaction of a polyunsaturated fatty acid, such as linoleic acid, has been regarded as a simple consecutive reaction:



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where L = linoleic acid (C18:2), O = oleic acid (C18:1), and S = stearic acid (C18:0). Geometric (*cis-trans*) isomers are not taken into account. Despite much research into the kinetics of this reaction, there is still doubt about the correctness of this scheme. Several researchers have concluded there is also a shunt reaction, which directly hydrogenates L into S (4,5). Consequently, such a shunt reaction limits the maximum selectivity of the reaction. An extensive review of the kinetics of this reaction is given by Veldsink *et al.* (1). They conclude that the kinetics of the reaction are still confusing, owing to the occurrence of several transport limitations, such as interfacial hydrogen transfer and intraparticle diffusion limitation.

For three-phase, consecutive reactions, transport limitations generally affect the selectivity of the reaction. The decreasing selectivity with increasing diffusion limitation of triglycerides or fatty acid methyl esters has been demonstrated for hydrogenation (6,7). The existence of intraparticle diffusion limitations can be calculated from the value of the Thiele modulus, which for a first-order reaction is (8):

$$\varphi = \frac{d_p}{6} \sqrt{\frac{k_1}{D_A^e}} \quad [2]$$

In Equation 2, k_1 denotes the first-order kinetic rate constant in s^{-1} , d_p is the catalyst dimension in m, and D_A^e expresses the effective diffusivity of the reactant in the catalyst in $m^2 s^{-1}$. Values for the effective diffusion coefficient were calculated by dividing the liquid-phase triglyceride diffusion coefficient (from Ref. 9) by 10 (1). For $\varphi < 0.2$, the reaction rate is slow in comparison with diffusional transport, and diffusion limitations are absent. Intraparticle diffusion limitation controls the rate of the overall conversion process if $\varphi > 2$.

Reduction of catalyst particle size is a direct way to reduce the influence of intraparticle diffusion limitation in slurry reactors (Eq. 2). However, for reasons of filtration efficiency, the particle diameter is usually limited to 5–10 μm . Instead of using smaller particles, it is also possible to use a structured catalyst in which the catalyst and reactants are present in a well-defined reaction zone. The present three-phase catalytic membrane reactor (3PhCMR) with hydrogen and liquid oil present on different sides of the catalytic membrane is an example of such a setup.

The present study examines the selectivity of hydrogenating vegetable oils in a catalytic membrane reactor. The catalytic interface separates hydrogen and liquid oil (Fig. 1). In the present setup, the catalyst is deposited in a very thin layer, $< 3 \mu m$. On one side of the catalyst the oil phase is flowing,

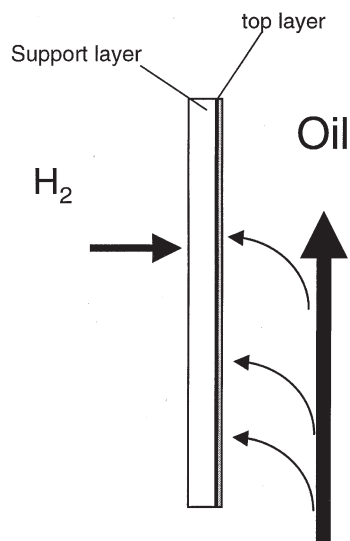


FIG. 1. Schematic representation of the three-phase catalytic membrane reactor (3PhCMR), with oil and H_2 fed on opposite sides of the membrane. The catalyst layer has a thickness of about $1\ \mu\text{m}$.

and triacylglycerol molecules will diffuse into the catalyst layer. On the opposite side, H_2 is present and will dissolve into the oil. This concept puts the active catalyst directly at the contact interface, thus reducing diffusion distances for the reactants and reducing transport limitations. Additional advantages are a highly flexible operation mode for the reactor and improved control of the selectivity by H_2 pressure, since a pressure increase will shift the contact interface to the liquid side. Hence, a 3PhCMR with separated feed of reactants offers an attractive alternative to slurry reactors for consecutive reactions with a high selectivity demand. In the present work, the hydrogenation of sunflower oil was used as a model reaction to study the concept of a 3PhCMR.

EXPERIMENTAL PROCEDURES

Materials. Refined, bleached and deodorized sunflower oil [iodine value (IV) = 133] was obtained from a local supermarket. Hydrogen gas was of 5.0 grade (Hoekloos, Dieren, The Netherlands). Commercial, cylindrical (α -)alumina membranes with a microporous top layer of approximately $1\ \mu\text{m}$ thickness (SCT, Bazet, France) were used. The microporous top layer was present at the tube-side of the membrane. Membranes with respective pore sizes of 5 and 20 nm were used. The 5-nm membranes had an alumina top layer, whereas the 20-nm membranes had a zirconia layer. Catalyst was deposited on the membrane by impregnation from a 1% PdCl_2 solution, followed by overnight drying at room temperature. This procedure was repeated once, and then the impregnated catalyst was reduced with hydrogen (5% H_2/N_2) at 300°C . Reduction was continued until HCl was no longer detected in the off-gas flow. Homogeneous distribution of Pd was verified by scanning electronic microscopy. Owing to the total weight of the membrane and inaccuracies in the impreg-

nation procedures, it was not possible to determine the catalyst load on the microporous top layer of the membrane.

Membrane reactor. The membrane was sealed into a stainless-steel housing. The housing had inlet and outlet connections on both the tube and shell sides. Oil was fed to the tube-side of the membrane, and H_2 was present at constant pressure on the shell side. A Pt-100 thermocouple was placed inside the tube to read the liquid temperature. Approximately 0.05 kg sunflower oil was filled in a well-stirred, round-bottom flask (100 mL). The temperature of the flask could be read from a thermometer, and samples could be taken from it by using a syringe. A pump circulated the oil through the tube. Both the flask and the membrane module were electrically heated and temperature-controlled. Thermometer readings of the oil passing through the membrane tube and in the flask were always within 2°C . Samples were taken at fixed intervals, and the amount of liquid sampled during hydrogenation was always less than 15%. Hence, no volume corrections were carried out in the calculations of the conversions. We verified that the conversion per pass through the membrane was below 0.02%, which means that the whole system could be mathematically described as a stirred-tank reactor (8). Furthermore, no gas bubbles were observed in the liquid phase during hydrogenation.

Analyses. Samples obtained from the 3PhCMR were first converted into their corresponding methyl esters and subsequently analysed by gas-liquid chromatography (GLC) using a 100-m SIL-88 column (Chrompack, Middelburg, The Netherlands). The injection port and column were maintained at 280 and 190°C , respectively, and split injection was used in a 1:4 split ratio. The analysis allowed for total *trans* fatty acid determination (10). IV were calculated from the chromatograms.

RESULTS AND DISCUSSION

Experiments with alumina membranes having 5-nm pores did not show any significant activity. After several days, the total IV-drop was still below 1%. GLC analysis showed that all hydrogenated fatty acids were directly converted into stearic acid, hence direct formation of tristearate was observed, which was confirmed by additional high-performance liquid chromatographic analysis. In contrast, normal hydrogenation runs were observed using the 20-nm zirconia membranes. In line with other work (11), we concluded that triglycerides do not enter the 5-nm pores. Consequently, the experiments were continued with the 20-nm zirconia membranes.

A typical plot of the fatty acid composition of the oil as a function of the conversion is shown in Figure 2. Conditions for the experiment were 74°C and 5 bar H_2 pressure. The horizontal axis plots the conversion of double bonds, which is defined as:

$$\zeta = 1 - \frac{x_{\text{MFA}} + 2 \cdot x_{\text{LA}}}{x_{\text{MFA}}^0 + 2 \cdot x_{\text{LA}}^0} = 1 - \frac{\text{IV}}{\text{IV}^0} \quad [3]$$

In this equation, ζ expresses the conversion, x the liquid molar fractions of monoenic fatty acids (MFA), i.e., C18:1 *cis*

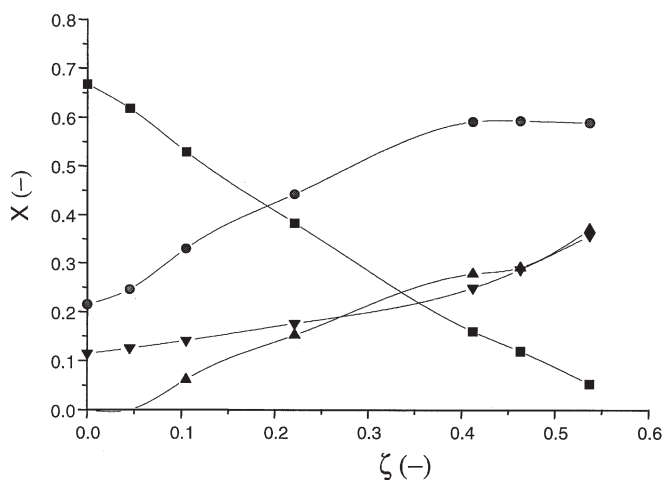


FIG. 2. Liquid phase composition in molar fraction, x , as a function of the conversion of double bonds, ζ , [iodine value (IV)-drop]. Conditions of the experiment: 74°C, 5 bar, 20 nm ZrO₂-membrane. From the experiment $S_I = 2.1$, and at $\zeta = 0.4$ (IV = 80) the level of *trans* = 0.26. Symbols: ■ = linoleic acid, ● = monoenoic fatty acids (C18:1 *cis* + *trans*), ▲ = C18:1 *trans*, ▼ = saturated fatty acid (C18:0).

and *trans*, and linoleic acid (LA). The superscript 0 refers to the initial conditions of the experiment. IV is the iodine number of the oil. At constant pressure, the selectivity is defined as the ratio of the first-order rate constants of the consecutive reaction scheme given in Equation 1:

$$S_I = \frac{k_L}{k_O} = \frac{\left(-1/x_L\right)\left(dx_L/dt\right)}{\left(1/x_M\right)\left(dx_S/dt\right)} \quad [4]$$

The selectivity of the experiment is $S_I = 2.1$ and at a conversion level of 40% of the double bonds (IV = 80), the level of *trans* = 0.26. Note that selectivity was calculated directly from the intercept of the respective transients plotted in Figure 2. Fitting of the curves and calculation of the values of the first-order rate constants were very poor. This can be attributed to the initial zero-order behavior of the disappearance of linoleic acid with conversion, the observed direct formation of saturated fatty acids, and the sigmoidal shape of the monoene transient. Similarly, hydrogenations at 86°C and 5 bar showed a selectivity of $S_I = 12.6$ and *trans* levels higher than 0.4 (IV = 80). The absence of intraparticle diffusion limitations of triglycerides was verified from Equation 2, which resulted in all cases in $\phi < 0.1$. Hence, the 3PhCMR behaves similarly to slurry catalysts with respect to the influence of temperature on selectivity and *trans* production.

In contrast with slurry reactors, a plot of the conversion as a function of the time at 86°C and 5 bar shows that there exists a conversion asymptote about and below 0.60 (Fig. 3), which is close to the theoretical value of $(1 - \zeta) = 0.57$ that would be found when the reaction was absolutely selective for linoleic acid. By allowing the 3PhCMR to continue to run for about 2 d, the hydrogen uptake indeed started to increase gradually when linoleic acid was absent. This indicated that absolute selectivity with respect to linoleic acid can be ob-

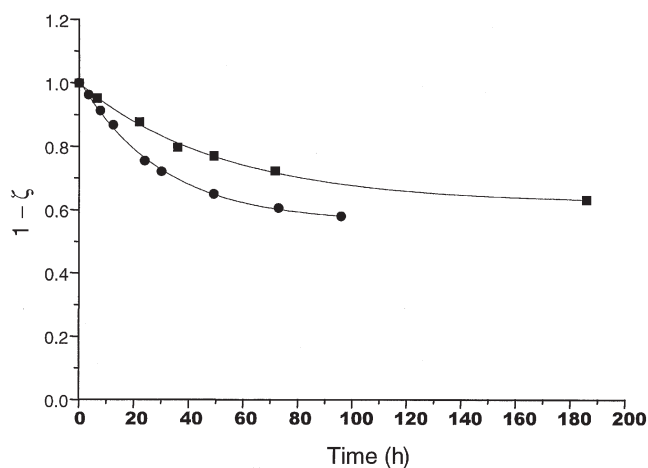


FIG. 3. Conversion $(1 - \zeta)$ of the double bonds as a function of time for hydrogenation of sunflower oil in the 3PhCMR using the 20-nm ZrO₂-membrane. Results are shown for the initial run (●) and for the run after 3 d of operation (■). Conditions: 86°C and 5 bar pressure. For abbreviation and symbols see Figures 1 and 2.

served in a three-phase catalytic membrane reactor. This has only been reported for Cu-catalyst. Probably, this can be explained from the fact that Pd-activity is much higher than Cu and, consequently, intraparticle diffusion limitations occur.

Figure 2 shows another remarkable characteristic of the 3PhCMR when plotting the conversion as a function of the run time for two consecutive hydrogenation runs. The rate of C18:1 *cis* and *trans* production equals the rate of *trans* production, which indicates a shunt reaction for the direct conversion of linoleic acid into stearic acid. Owing to the fact that intraparticle diffusion limitations influenced the experimental results, the existence of the shunt reaction could never be unambiguously demonstrated in the liquid phase. Supporting evidence was only obtained for vapor-phase reactions (12). We concluded that, over Pd catalyst and under selective conditions, the hydrogenation of linoleic acid primarily yields C18:1 *trans* and stearic acid and no production of oleic acid occurs. This can be mechanistically explained by postulating a conjugated surface intermediate (1,13–15).

The influence of pressure was studied for the 3PhCMR, although only over a relatively narrow range of H₂ pressures, 3–5 bar. We found negligible influence of H₂ pressure on the conversions and H₂ fluxes. Although the pressure interval was narrow, it definitely showed that interfacial transport of hydrogen was not limiting, which would result in a linear dependence of the H₂ flux on pressure. Furthermore, the absence of a pressure influence over a limited pressure range can be explained from absorption-type kinetics, such as described by Langmuir-Hinshelwood-type rate equations (1).

In Figure 4 are plots of the conversion of several hydrogenation runs in the 3PhCMR as a function of time. Also the interfacial hydrogen flux, calculated from

$$J_{H_2} = -k_L a_{He} P_{H_2} \quad (\text{mol m}^{-3} \text{ s}^{-1}) \quad [5]$$

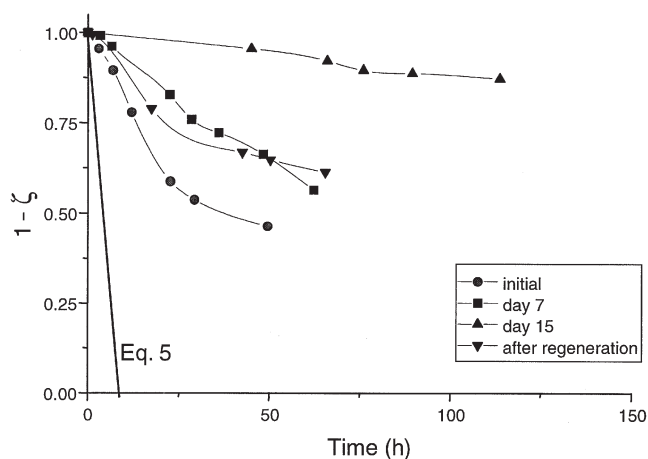


FIG. 4. Conversion ($1 - \zeta$) as a function of time for hydrogenation of sunflower oil over Pd in 3PhCMR. Runs illustrate the loss of activity as a function of time and subsequent partial activity recovery after regeneration. For comparison, the interfacial hydrogen flux, as calculated from Equation 5, is also plotted in the graph. For abbreviation and symbols see Figures 1 and 2.

is plotted in the same diagram. In Equation 5, $k_L a$ stands for the volumetric, interfacial, hydrogen mass transfer coefficient (s^{-1}), H_e is the Henry coefficient ($\text{mol bar}^{-1} \text{m}^{-3}$), and P_{H_2} is the hydrogen pressure in bars. By comparing the calculated interfacial flux and the experimental conversion transients, we concluded that the fluxes were not limited by interfacial transport by more than 15%. Furthermore, Figure 4 shows that the catalyst activity of the 3PhCMR decreases with increasing hydrogenation runs (or time). Fractional regeneration of the catalyst activity appears to be possible by exposing the membrane at 450°C in air for 6 h. However, after two regenerations, catalyst activity was totally absent and could not be recovered.

This study presents hydrogenation of sunflower oil in a novel membrane reactor. Owing to the thin layer of catalyst, transport limitations can be avoided in the membrane reactor. Furthermore, the 3PhCMR is easy to scale up and has a flexible operation window. However, regeneration procedures should be further developed before a 3PhCMR can be operated commercially.

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