Deactivation and Coke Formation on Palladium and Platinum Catalysts in Vegetable Oil Hydrogenation

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ABSTRACT: Deactivation of palladium and platinum catalysts due to coke formation was studied during hydrogenation of methyl esters of sunflower oil. The supported metal catalysts were prepared by impregnating γ-alumina with either palladium or platinum salts, and by impregnating α-alumina with palladium salt. The catalysts were reused for several batch experiments. The Pd/γ-Al_2O_3 catalyst lost more than 50% of its initial activity after four batch experiments, while the other catalysts did not deactivate. Samples of used catalysts were cleaned from remaining oil by repeated extractions with methanol, and the amount of coke formed on the catalysts was studied by temperature-programmed oxidation. The deactivation of the catalyst is a function of both the metal and the support. The amount of coke increased on the Pd/γ-Al_2O_3 catalyst with repeated use, but the amount of coke remained approximately constant for the Pt/γ-Al_2O_3 catalyst. Virtually no coke was detected on the Pd/α-Al_2O_3 catalyst. The formation of coke on Pd/α-Al_2O_3 may be slower than on the Pd/γ-Al_2O_3 owing to the carrier's smaller surface area and less acidic character. The absence of deactivation for the Pt/γ-Al_2O_3 catalyst may be explained by slower formation of coke precursors on platinum compared to palladium.

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KEY WORDS: Catalysis, coke, deactivation, hydrogenation, methanol extraction, methyl ester of sunflower oil, Pd/α-Al_2O_3, Pd/γ-Al_2O_3, Pt/γ-Al_2O_3, temperature-programmed oxidation (TPO).

Different metal catalysts have been studied as alternatives to nickel catalysts for edible oil hydrogenation, but very few data are published on the kinetics of triglyceride or fatty acid methyl ester (FAME) hydrogenation for palladium or platinum catalysts (1). Platinum in general forms less *trans*-isomers during hydrogenation than nickel but has a poorer selectivity for hydrogenation of polyunsaturated fatty acids. Palladium is more selective than nickel catalysts for hydrogenation of polyunsaturated fatty acids but forms more *trans*-isomers during a typical hydrogenation.

To avoid losses of the precious metals during hydrogenation, a fixed bed reactor may be an attractive alternative to the stirred batch reactors used today for most oil hydrogenations with nickel catalysts. Poisoning and deactivation is a larger problem for fixed bed reactors, unless there is an easy way to regenerate the catalyst, preferentially *in situ*. Catalyst deactivation in oil hydrogenation is often caused by poisoning by sulfur or other components present in the oil. Even if all poisons are removed, catalyst deactivation may also be caused by side reactions during the hydrogenation that lead to intermediates or products, such as carbon monoxide (2) or carbonaceous deposits (coke), that may lower the catalyst activity. Coke is often readily formed on catalysts during hydrogenation reactions (3), but coke formation as a cause for catalyst deactivation has not been reported in edible oil hydrogenation. Coke usually causes activity decay by blocking active sites or plugging the porous system. Yet, coke sometimes has a more complex role. Coke can be more or less harmful, and the carbonaceous layer may even be the site where the reaction takes place (4). Coke formation is usually associated with high-temperature gas-phase reactions. However, deactivation by coke formation has also been observed during processes carried out at moderate and low temperatures, such as the liquid-phase hydrogenation of acetylene (5).

Temperature-programmed oxidation (TPO) is a method that has been widely used to study catalysts deactivated by coke formation (6). The coked sample is placed in a reactor and heated, usually following a linear ramp, in an atmosphere containing oxygen. The consumption of oxygen and the formation of carbon dioxide and water are monitored by, for example, a mass spectrometer. By this method, it is possible to measure the total amount of coke on the catalyst and to determine the hydrogen-to-carbon ratio of the coke. It is also possible to obtain information on the location of the coke on the catalyst surface by observing the different peaks obtained during the combustion.

The aim of this study was to examine the stability of supported palladium and platinum catalysts during hydrogenation of vegetable oils. By using TPO, we also wanted to investigate the role of coke in the deactivation process.

EXPERIMENTAL PROCEDURES

Catalyst preparation and characterization. Palladium catalysts were made by impregnating palladium nitrate on commercial γ-Al_2O_3 (Girdler T-126, Tokyo, Japan) or α-Al_2O_3 (Süd-Chemie T-1571, Munich, Germany) support. Pellets of the support were crushed and sieved to a particle size of 32–71 µm. The supports were stabilized for 4 h at 600°C. An incipient wetness method (7) was used to impregnate the

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metal salt on the carrier. The impregnated catalysts were dried for about 24 h at 120°C to crystallize the salt. The catalysts were calcined at 300°C in air (300 mL/min) for 5 h and reduced at 300°C in hydrogen (200 mL/min) for 5 h.

The platinum catalyst was prepared by impregnating platinum chloride on γ-Al_2O_3 (Girdler T-126). Further information is found elsewhere (8).

Metal contents of the catalysts (Table 1) were measured by atomic absorption spectroscopy (Varian SpektrAA-10; Varian, Mulgrave, Australia). Chemisorption of carbon monoxide, measured by an Ami 100 (Zeton Altamira, Pittsburgh, PA), was used to estimate the metal dispersion in the catalyst. With this fully automated catalyst characterization system, measurements were made by observing the adsorption of pulses of CO in He using a thermal conductivity detector for determining the CO concentration at the gas outlet. Since the CO/metal stoichiometry depends on the dispersion of the metal, the method will only give approximate values for the metal dispersion (9).

Reactant composition. The FAME used in the experiments were prepared by Unilever Research Laboratories (Vlaardingen, The Netherlands). The composition of the FAME was 66.5% methyl linoleate (C18:2, 9-*cis*,12-*cis*), 20.8% methyl oleate (C18:1 9-*cis*), 5.1% methyl stearate (C18:0), 6.6% methyl palmitate (C16:0), and less than 1% of methyl arachidate (C20:0) and methyl behenate (C22:0). No sulfur was detected in the oil (Tractor Atlas 825/856, Tomball, TX; detection limit 0.1 ppm).

Hydrogenation experiments. The reactor used for hydrogenation experiments was a 1000-mL stirred slurry tank reactor operating in a semi-batch mode (continuous hydrogen flow). Inlet (N_2, H_2) and outlet flows and reactor pressure were all electronically measured (Bronkhorst HI-TEC, Ruurlo, The Netherlands). The pressure, temperature, and gas flows were controlled by a computer.

The experiments were started by loading the catalyst, about 5 g, into the reactor. To avoid any induction period due to partial oxidation of the reduced catalyst, the catalyst was first exposed to a hydrogen atmosphere for 2 h at 150°C. About 400 g of FAME was introduced to the reactor.

Agitation (2500 rpm), heating, and nitrogen flow (500 mL/min) were turned on after introducing the FAME. Hydrogenation was performed at 80°C with an atmospheric pressure of H_2 with catalyst Pd-A, and at 80°C and 2 bars H_2 pressure for Pd-B (see Table 1 for differences between catalysts). Owing to reaction rates that were too high, where mass transfer limitations may mask the deactivation, the experimental conditions were changed to 60°C and 2 bars H_2 pressure for the further experiments with catalyst Pd-B, Pd-α, and Pt. The reaction conditions were stabilized for 20 min before the reaction was started by changing the nitrogen flow to hydrogen (2300 mL/min). During the experiment, the extent of hydrogenation was determined by measuring the refractive index of the FAME. The hydrogenation rate was also observed as the direct uptake of H_2. These measurements were used for determining the appropriate liquid sampling interval.

TABLE 1
Catalyst Characterization

Catalyst	Formulation	Metal loading (%)	Chemisorbed CO[a] (μmol/g catalyst)	Chemisorbed CO (mol/mol metal)
Pd-A	Pd/γ-Al_2O_3	0.84	11.3	0.143
Pd-B	Pd/γ-Al_2O_3	0.086	1.9	0.238
Pd-α	Pd/α-Al_2O_3	0.10		
Pt	Pt/γ-Al_2O_3	0.68	3.1	0.09

[a]Measured by pulse chemisorption.

The reaction rates used in the modeling were calculated from gas chromatographic analysis. Liquid samples, which were taken during the hydrogenation, were analyzed with respect to the FAME composition by a Varian 3400 CX gas chromatograph (Walnut Creek, CA) equipped with a CP-SIL 88 column (100 m × 0.25 mm, Chrompack, Middelburg, The Netherlands) operated isothermally at 165°C. The FAME were separated by carbon chain length, (C16–C22), by number of double bonds (0–2), by double-bond position along the carbon chain (7–15), and by *cis-trans* configuration. Overlapping of the peaks occurred between *trans*-isomers with a single double bond in a high position (>11) and *cis*-isomers with a single double bond in a low position (<9). The C18:1 peaks appearing before C-18, 9-*cis* were lumped into C-18:1 *trans*-isomers (T) and the C18:1 peaks appearing later into C-18:1 *cis* (C).

The hydrogenation was stopped at similar conditions at each run, corresponding to a state where most of the FAME with two double bonds had been hydrogenated. The catalyst samples were taken for the TPO experiments at the end of the hydrogenations. The reaction was stopped by turning the agitation off and cooling the oil in a nitrogen flow. The oil was removed after the catalyst had settled. The reactor was then refilled with fresh oil, keeping the oil-to-catalyst ratio constant. Four separate runs were performed using the same catalyst. Before the first experiment in each batch series, a catalyst sample was also taken after the heating period prior to the start of the hydrogenation.

Extraction methods. The coke content of the catalyst was determined by oxidizing the carbonaceous residues on the catalyst. Accurate results will be obtained only if the remaining oil is removed from the catalyst before the oxidation. The aim of the extraction was to remove the remaining oil from catalyst pores, without dissolving the coke or changing its composition. Different methods and solvents were tested and compared in order to fulfill these requirements.

To verify if the selected method could remove oil from the catalyst pores, pure γ-Al_2O_3 support and fresh Pd-A were immersed in oil for periods of less than a minute at room temperature. It was assumed that the rate of coke formation was very slow at room temperature and that the time period was so short that all hydrocarbons around and inside the catalyst could be classified as oil and should therefore be possible to remove by extraction. The solubility of the coke was examined by extracting the used Pd-A catalyst with different methods and measuring the coke content by TPO.

Two extraction methods, “solvent extraction” and “Soxhlet extraction,” and two solvents, hexane and methanol, were investigated. Hexane has been used as a solvent in industrial extraction applications with vegetable oil (10), and methanol is a commonly used solvent in both extraction methods.

The catalyst, about 0.2 g, was flushed with the selected solvent prior to the extraction. In solvent extraction, the catalyst sample was then extracted in 15 mL of fresh solvent four consecutive times. This was done in an ultrasonic bath at 0 or 25°C using varying extraction periods (4 × 5—45 min). Soxhlet extraction (11) was used with 25 mL of hexane or methanol as the condensing solvents.

The extracted catalysts were dried in a furnace at 120°C in an air atmosphere after the extraction. The different combinations of solvents and methods that were used are reported in Table 2.

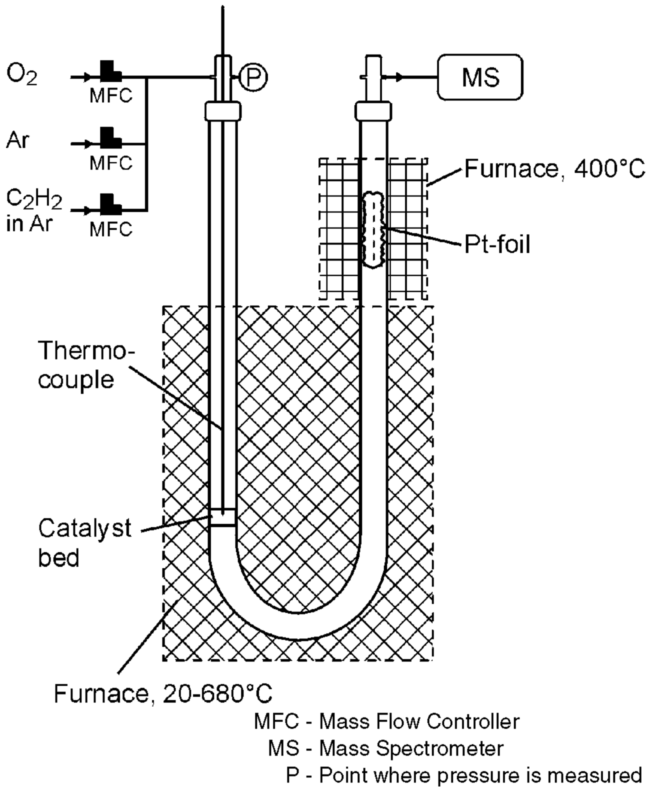
Influence of startup conditions on coke formation. The catalyst surface reportedly is covered by carbonaceous species almost immediately after exposure to hydrocarbons (8), and the initial deposition of coke has been shown to be dependent on temperature (12). Hence, it can be assumed that coke formation occurs as soon as the catalyst is mixed with the oil and continues during the whole heating period at the startup of the hydrogenation experiments. A study was made where the effects of temperature and exposure time on the coke formation were investigated. The study was carried out in the absence of hydrogen in order to study the behavior of the components without simultaneous hydrogenation reactions.

The experiments were performed by filling a glass bottle with 30 mL of fresh oil, which was agitated by a magnetic stirrer and heated to the desired temperature by an electric heater. Approximately 0.20 g of catalyst was introduced to the oil, and different contact times (5–60 min) and temperatures (20–80°C) were examined. The experiments were ended by turning off the agitation and by cooling the oil to 0°C in an ice-water bath. The catalysts (Pd-B and Pt) and support (γ-Al_2O_3) were then extracted by solvent extraction with methanol and the coke content was measured by TPO.

TPO. Scheme 1 shows the reactor system used for the TPO experiments. The reactor consisted of a U-formed quartz tube. After the main oven, a second oven heated the last part of the reactor containing a platinum foil. The temperature in this oven was kept at 400°C during the whole experiment; and desorbing, partially uncombusted, hydrocarbons were oxidized completely to carbon dioxide and water.

TABLE 2
Measured Coke Contents

	Extraction procedure		Coke content (wt%)		
Solvent	Extraction method	Extraction time	Support (γ-Al_2O_3)	Fresh Pd-A	Used Pd-A
Methanol	Solvent	4 × 5 min	1.9	0.7	8.6
	Soxhlet	3.5 h	2.4	1.4	6.6
		2 × 3 h	2.5		
Hexane	Solvent	4 × 5 min	6.5	7.1	9.9
	Soxhlet	3.5 h		6.4	8.8
		2 × 3 h	10.4		
		2 × 4 h	9.9		

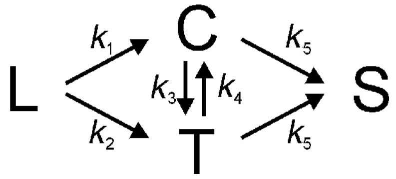


SCHEME 1

The flow rates of the gases (Ar, O_2, and a mixture of C_2H_2 in Ar) were regulated by mass flow controllers (Bronkhorst HI-TEC). A mass spectrometer (Gaslab 300; Fison Instruments, Middlewich, England) was used to study the gases formed during the combustion.

Catalysts (30–50 mg) were placed in the TPO reactor after extraction and drying. The catalyst bed was diluted with crushed quartz beads in order to prevent ignition of the catalyst due to the heat formed by the oxidation of the coke. A mixture of 21 mL/min Ar and 4 mL/min O_2 was used. The temperature in the reactor was increased from room temperature to 680°C at a heating rate of 10°C/min. After each TPO experiment, the signals were calibrated by burning the acetylene mixture.

Kinetic modeling. The aim of the kinetic modeling was only to find a hydrogenation model that could well describe the experimental observation and then to add terms to that model in order to include the deactivation of the catalyst. A model based on Langmuir-Hinshelwood kinetics was fitted to the experimental data. Most rate data on heterogeneous catalysts are accurately represented *via* a Langmuir-Hinshelwood rate equation (13), and similar models have been used by other authors for hydrogenation both with nickel catalysts and with palladium catalysts (14–17). The oil compounds were



SCHEME 2

lumped into four groups for the modeling (Scheme 2), where L is all di-unsaturated components (linoleic); T is mono-unsaturated with a *trans* double bond; C is mono-unsaturated with a *cis* double bond, and S is the saturated fraction. C and T form at different rates from the L fraction (k_1 and k_2 in Scheme 2). The model included *cis-trans* isomerization of the monounsaturated components (k_3 and k_4), but not double-bond migration. C and T react equally fast to S (k_5) in the model. The effect of the hydrogen concentration was not included in the kinetic model as the hydrogen pressure was kept constant in each series of experiments, and the solubility of hydrogen was assumed not to change during the course of reaction. The following assumptions were made for the reaction rates: (i) adsorption equilibrium between the reactants in the liquid phase and on the catalyst surface; (ii) no adsorption of the saturated product on the catalyst surface; (iii) *cis* and *trans* isomers adsorb equally strong; (iv) the adsorption of the hydrogen is assumed to occur independently of the oil compounds due to the difference in molecular size.

By using these assumptions, the reaction rates may be written as:

$$r_1 = \gamma(t)\frac{k_1 c_L}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [1]$$

$$r_2 = \gamma(t)\frac{k_2 c_L}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [2]$$

$$r_3 = \gamma(t)\frac{k_3 c_C}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [3]$$

$$r_4 = \gamma(t)\frac{k_4 c_T}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [4]$$

$$r_5 = \gamma(t)\frac{k_5 c_C}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [5]$$

$$r_6 = \gamma(t)\frac{k_5 cT}{\left[1 + K_L c_L + K_M\left(c_C + c_T\right)\right]} \qquad [6]$$

where K_L and K_M are the equilibrium adsorption constants for the di-unsaturated and the mono-unsaturated components, respectively. The terms k_1–k_5 are lumped rate constants. They are the products of the kinetic rate constant and the equilibrium adsorption constant for the reactant.

The deactivation was separated from the hydrogenation kinetics using the activity parameter γ, which was modeled to be a function of time only, independent of reaction conditions. γ was modeled as $\gamma = e^{(-\alpha t)}$, $\gamma = 1/(1 + \alpha t)$, $\gamma = 1 - \alpha t$ or as being equal to unity (no deactivation). Using a single γ for all reactions means that the model does not allow for changes in selectivity with increased deactivation. The activity and the kinetic parameters were fitted simultaneously to the data. The nonlinear least-squares regression was solved using a Levenberg-Marquardt routine in the MATLAB (The Mathworks, Natick, MA) software package.

RESULTS AND DISCUSSION

Hydrogenation experiments. Figure 1 shows the experimental results and the model fitted to the data for the experiments conducted at 60°C. It was found that the palladium supported on γ-Al_2O_3 catalyst deactivated. This was not the case for the other catalysts. The palladium on α-Al_2O_3 became more active during the first batch experiment and then held a constant activity for the following batch experiments. The activity was constant in all batches for the platinum catalyst.

The experiments showed that there was no change in relative *trans*-isomer formation or in selectivity of the hydrogenation of di-unsaturated components for the deactivating Pd-B catalysts with reaction time. This made it possible to use a deactivation model with a single γ for all the reactions. The deactivation of the Pd-B catalyst was modeled using different expressions for the activity γ. Owing to the rather low degree of deactivation, all the models including deactivation worked equally well. The results from the modeling are shown in Figure 1 using $\gamma = e^{(-\alpha t)}$ for Pd-B and without deactivation ($\gamma = 1$) for the other two catalysts. It was possible to fit the Langmuir-Hinshelwood kinetic model well to the experimental data for all catalysts.

The formation of *trans*-isomers was much lower for the platinum catalyst than for the palladium catalysts. This behavior for platinum and palladium has previously been reported in the literature, both for vegetable oil hydrogenation (1,18,19) and for alkene hydrogenation in general (20). The selectivity for hydrogenation of linoleic acid was higher for the palladium catalysts than for the platinum catalyst.

Mass transport limitations. Deactivation and kinetics should preferably be studied in the absence of mass transport limitations. The volumetric mass transfer coefficient, $k_l a$, was determined to be 0.61 s^{-1} in separate experiments using an excess of catalyst. The reaction rate may then be set equal to the mass transfer of hydrogen through the liquid film

$$r_{H_2} = k_l a\left(\frac{p_{H_2}}{\mathrm{He}} - c_{H_2,b}\right) \qquad [7]$$

where r_{H_2} is the total reaction rate for the hydrogenation reactions per m^3 liquid, p_{H_2} the gas phase pressure of hydrogen, He the Henry's law constant, and $c_{H_2,b}$ the bulk concentration of hydrogen in the liquid phase. The $k_l a$ value of 0.61 s^{-1} corresponds to a concentration gradient over the gas–liquid interface of less than 15% at the highest reaction rate obtained in the experiments.

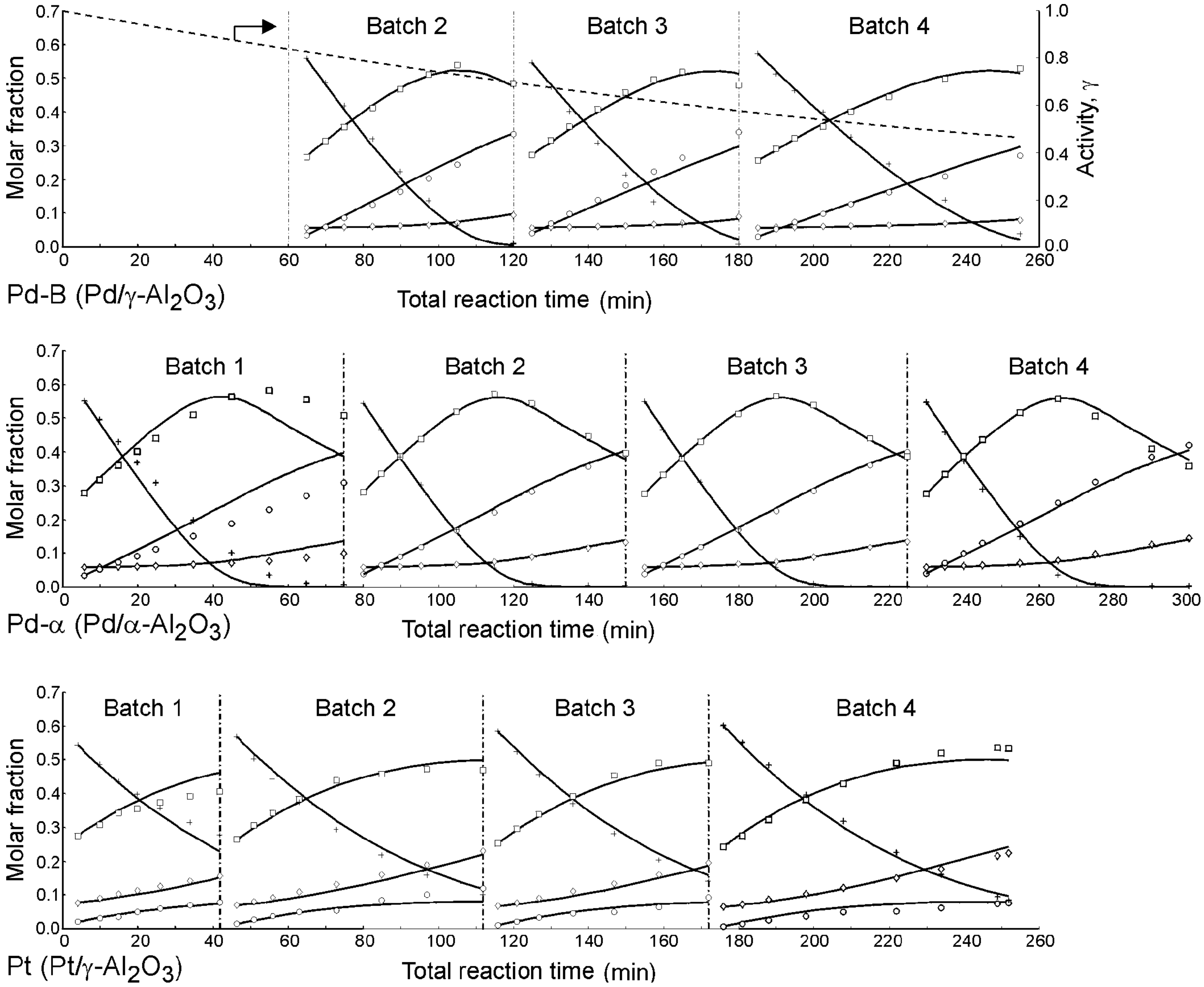


FIG. 1. Hydrogenations using Pd-B, Pd-α, and Pt catalysts. The solid lines indicate the fitted model, and the symbols indicate the measured data; (+) L (di-unsaturated components), (□) C (mono-unsaturated, *cis*-double bond), (○) T (mono-unsaturated, *trans*-double bond), (◇) S (saturated). Batch 1 for Pd-B was not used in the model due to problems with the stirrer. For Pd-B, deactivation has been incorporated into the model. The activity γ is indicated by a dotted line. The reaction rates for the other catalysts have been modeled assuming constant activity of the catalyst. Pd-α became more active after the first run. Therefore, the model for this catalyst was obtained using only batches 2–4.

The Weisz modulus, Φ, is commonly used for estimating the effect of pore diffusional limitations. It may be calculated as

$$\Phi = \frac{r_v r_p^2}{D_{\text{eff}} c_s} \qquad [8]$$

where r_v is the reaction rate per volume of catalyst, r_p the catalyst radius, D_{eff} the effective diffusivity of the reactant inside the catalyst, and c_s the reactant concentration at the catalyst perimeter. It is difficult to obtain a reliable value for D_{eff} for both hydrogen and the FAME. Tsuto *et al.* (17) estimated the effective diffusivity of hydrogen in methyl linoleate hydrogenation on a Pd-on-carbon catalyst to be 3.6×10^{-9} m^2/s at 80°C. By using the Stokes-Einstein relationship

$$\frac{DT}{\mu} = \text{const} \qquad [9]$$

and viscosity data for methyl oleate (21), this corresponds to an effective diffusivity of 2.6×10^{-9} m^2/s at 60°C.

The lowest effectiveness factors occur in the largest catalyst particles (d_p = 71 μm) at the highest reaction rates observed during the experiments. The Weisz modulus with respect to hydrogen transfer at those conditions is 8.7, which corresponds to an effectiveness factor of 0.57 for a first-order reaction in a spherical particle.

The pore diffusion resistance for the FAME also may be calculated using a bulk diffusivity of 6×10^{-10} m^2/s (22). Combining Equations 7 and 9 gives a Weisz modulus of 0.87

for hydrogenation of the di-unsaturated component, and a corresponding effectiveness factor of 0.94.

The external mass transfer from the gas phase to the liquid phase had only a small influence on the reaction rate, and it affected all the experiments in a similar way because of the similar reaction rates. The effect of internal mass transfer resistance in the catalyst pores was not negligible. However, even at the highest initial reaction rates the efficiency factor for hydrogen was about 0.5 for the largest catalyst particles, assuming the reaction to be first order with respect to hydrogen. Mass transfer limitations will mask, not enhance, the deactivation of the catalyst, as long as the coke formation in itself does not hinder the mass transfer. We believe that the coke formed in these reactions is similar to the reactants and that the coke formation in itself has no major effect on the mass transport. An efficiency factor of 0.57 is not negligible and will affect the values of the parameters for the fitted models. The observed deactivation of the Pd/γ-Al_2O_3 catalyst is probably somewhat smaller than the true deactivation. This is caused by the higher efficiency factor for the catalysts that is obtained at the lower (deactivated) reaction rates, thereby eliminating a part of the deactivation effect.

Extraction methods. A series of experiments was carried out in order to discover which extraction method was the most appropriate. After the extraction, the coke content was analyzed by running TPO. Experiments with fresh catalysts (support and Pd-A) that were in brief contact with oil showed that hexane was not able to remove the oil from catalyst pores at room temperature (6.5–10.4% remaining, see Table 2). Methanol, on the other hand, removed more of the oil from the catalysts with both solvent and Soxhlet extraction (0.7–2.5% oil remaining). The study showed that some hydrocarbons were always retained on the samples with the investigated methods. However, solvent extraction with methanol reduced the amount to a low level.

Analysis of the coke concentration of the Pd-A catalyst used in four consecutive hydrogenations gave the same result after solvent extraction with methanol (8.6%) and after using Soxhlet extraction with hexane (8.8%). When samples of the used Pd-A catalyst were extracted with hexane, that the estimated coke concentration after Soxhlet extraction (8.8%) was found to be lower than after solvent extraction (9.9%). An explanation could be the increased solubility of the oil in hexane at higher temperature (b.p. for hexane 69°C) during the Soxhlet extraction. When methanol was used, the Soxhlet extraction also resulted in a lower observed coke content (6.6%) than after solvent extraction, indicating that not only the oil in the catalyst but also some of the coke was removed. Soxhlet extraction with methanol has been reported to solvate a substantial part of the coke from a used catalyst (23).

Different extraction temperatures and durations were tested for solvent extraction with methanol, but no significant differences in coke content were noticed. Nor did increased extraction time or number of extraction cycles have any significant influence on Soxhlet extraction with methanol.

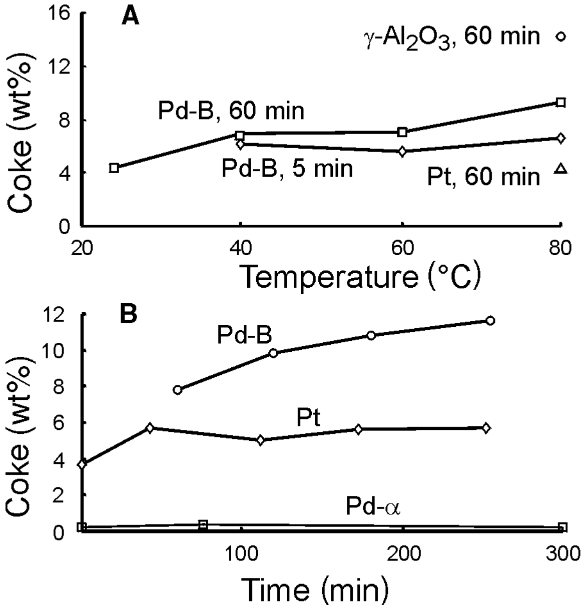


FIG. 2. (A) Measured coke content on samples contacted with oil for various times and temperatures. (B) Coke formation on the catalysts vs. time on-stream. Each symbol indicates one batch. The coke concentration was not analyzed for the Pd-α-Al_2O_3 catalyst after batches 2 and 3. The other two curves represent catalysts on γ-Al_2O_3 support.

Analysis of Pd-B in contact with oil without performing the hydrogenation reaction showed that the coke content increased both with increased temperature and with increased contact time (Fig. 2A). Pure γ-Al_2O_3 support was immersed in oil for 60 min at 80°C. The observed coke concentration was larger than for the palladium catalyst exposed to the same treatment. The coke concentration was much lower on the platinum catalyst after the same treatment. The result showed that it would be essential to do extraction at a low temperature and to minimize the catalyst contact time with oil after the hydrogenation in order to reduce coke formation during the extraction.

The criteria for choosing the extraction method were the following: (i) A low amount of residual oil should be found on a fresh catalyst. (ii) The method should remove as little coke as possible from the used catalyst, while still removing all the oil in the pores (criterion i). (iii) The method should be easy to perform, ensuring high reproducibility.

Based on the above-mentioned results, the chosen method, which was used to prepare the hydrogenation catalyst samples for the TPO studies, consisted of solvent extraction with methanol in four steps (4 × 5 min) in an ice-water bath.

Definition of coke. It is more difficult to define coke for liquid-phase reactions than for gas-phase reactions, especially for liquids with a high boiling point. The estimated amount of coke is dependent on the method used to analyze the carbonaceous deposits. In the present context we refer to coke as all the species that were not removed by solvent extraction using methanol. This may also include reactants strongly adsorbed on the metal or on the support, as well as the more dehydrogenated species present on the catalyst.

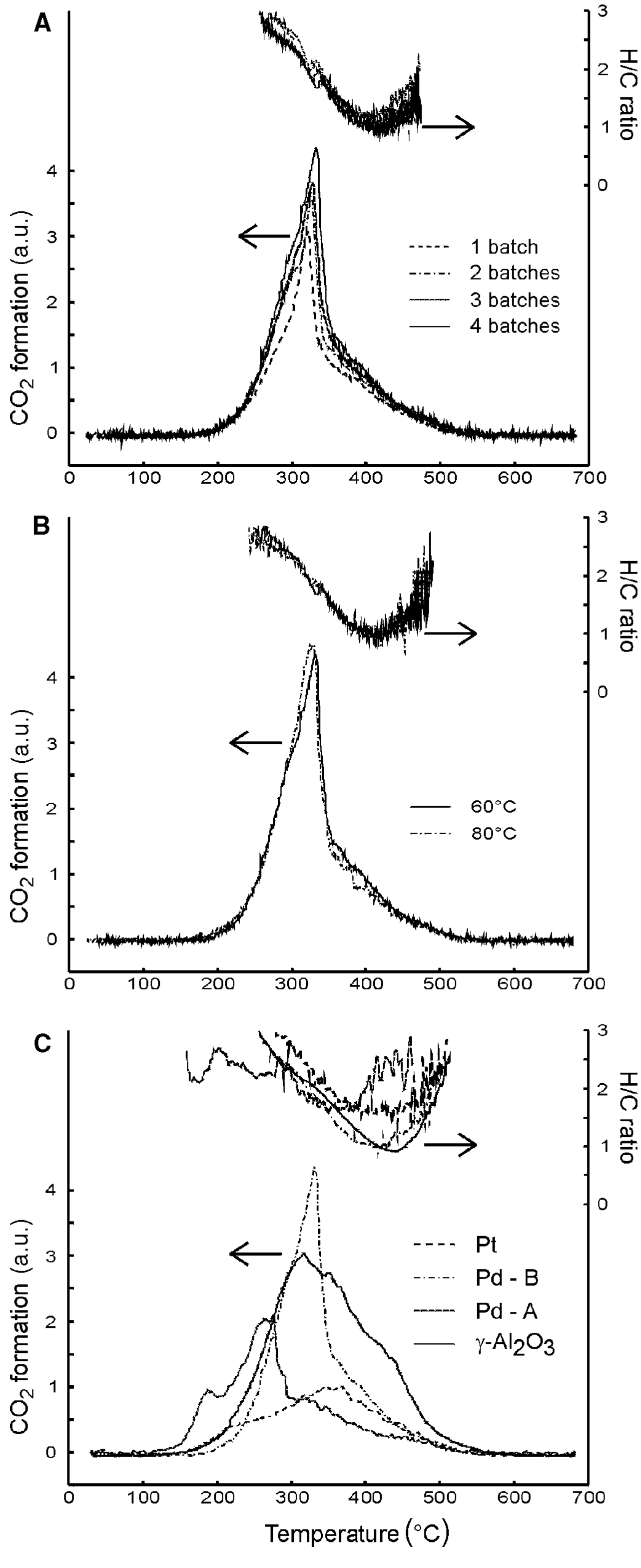


FIG. 3. Temperature-programmed oxidation profiles and the hydrogen-to-carbon (H/C) ratio for three different reaction systems. (A) Pd-B catalyst deactivated during four consecutive oil hydrogenation batches at 60°C. (B) Comparison between Pd-B catalyst after four consecutive hydrogenation batches at 60 and 80°C. (C) Pure γ-Al_2O_3 support (contacted with oil for 60 min at 80°C), and catalysts Pd-A, Pd-B, and Pt. The catalysts were used in four consecutive hydrogenation batches at 80°C (Pd-A) and 60°C (Pd-B and Pt).

The amount of coke formed on the used catalysts. Figure 2B shows how the coke content varies with time on-stream for catalysts Pd-B, Pd-α, and Pt at hydrogenation runs at 60°C. Each symbol indicates one batch. The catalyst was mixed with oil and heated before the reaction was started. This resulted in coke accumulation on the catalyst. The amount of coke accumulated on the Pd/γ-Al_2O_3 catalyst increased with time. The Pt/γ-Al_2O_3 catalyst contained less coke and the amount of coke did not increase with time except for the first batch. Only very small amounts of carbonaceous residues accumulated on the Pd/α-Al_2O_3.

TPO profiles obtained from coke on used catalysts. Figures 3A and 3B show typical results from runs performed with Pd-B. The plots in Figure 3A show that the amount of hydrocarbons retained on the catalyst increased with the number of oil hydrogenation batches without any changes in the characteristics of the profiles of the TPO curves. In Figure 3B a comparison is shown between runs at 60 and 80°C, again without any indications that the coke is different apart from the amount of coke. The hydrogen-to-carbon ratio (H/C ratio) is also shown in Figure 3. The most important observation made from the TPO curves is the similarity between the profiles despite different reaction temperature and time on-stream.

However, when comparing the TPO curves obtained from the experiments in which the Pd-B catalyst was immersed in oil (not shown here) with the curves presented in Figures 3A and 3B, it is possible to see a small shift toward higher temperature for the catalysts used in the hydrogenation.

The effect of catalyst formulation on the TPO profiles is illustrated in Figure 3C. The peaks move to lower temperatures with higher metal loading for the Pd catalysts. The profile from the Pt catalyst consists of two peaks distributed over a rather broad temperature range. One broad peak is observed for the pure γ-alumina support. The H/C ratio for the coke also differs with catalyst formulation. The catalysts with high metal loading (Pd-A and Pt) have a more evenly distributed H/C ratio over the whole temperature range.

Formation of the coke and its characteristics. After only a very short time, carbonaceous residues are formed on the catalysts. The experiments shown in Figure 2A demonstrate that a large amount of coke also is formed in the absence of hydrogen.

Pure carrier that was exposed to the same treatment in oil as the supported metal catalysts (60 min at 80°C) contained more coke (Fig. 2A). The results indicate that the more metal on the catalyst, the less coke is formed. An explanation for this observation is that the most acidic sites on the support are eliminated during the preparation. A more acidic carrier is known to give rise to a higher coke formation rate (24).

The origin of the peaks in TPO profiles has been discussed by Parera *et al.* (25). They concluded that peaks at low temperatures originate from coke on and near the metal, and that the oxidation is catalyzed by the metal. Peaks appearing at higher temperatures are caused by coke on the carrier. A higher metal loading will result in combustion at lower temperatures, as observed in Figure 3C.

A shift to a higher temperature for the peak maximum was observed when comparing the catalysts used during the hydrogenation reaction with the catalysts immersed in oil, indicating a more strongly bound carbonaceous deposit in the former case. This can be explained by changes in the characteristics of the coke caused by a longer exposure time to oil, or by the presence of hydrogen.

The H/C ratios in the coke are compared for the same palladium catalyst deactivated for different times (Fig. 3A) and at different temperatures (Fig. 3B). The H/C ratios are independent of the different coking conditions. The very high H/C ratio in the first part of the peak in Figures 3A and 3B, and the increased ratio at the end, can be explained by water desorbing from the support. The H/C ratio for the main part of the coke combustion decreased from about 2.5 to 1, and this change can be explained by the fact that coke burned at the end of the peak is more dehydrogenated than coke burned in the beginning (26). The H/C ratios differ, however, for the coked catalysts with various compositions. The coke obtained on the catalysts with a higher metal loading has a higher H/C ratio for the coke burned off between 300–400°C than the coke on the pure alumina support and on the palladium catalyst with a lower metal loading. We may therefore conclude that this coke is more dehydrogenated in the latter case than on the high metal loading catalysts.

Deactivation due to coke formation. Deactivation of the catalyst and coke accumulation was found to occur simultaneously on the palladium catalyst supported on γ-Al_2O_3. The mechanism for deactivation by coke formation, in our case, must include both the metal and the support. Otherwise, deactivation should have been observed either on the platinum catalyst supported on γ-Al_2O_3 or on the palladium catalyst supported on α-Al_2O_3.

Trans-isomerization was found to be considerably higher on the palladium than on the platinum catalyst. The faster formation of *trans*-isomers and the higher selectivity for linoleate hydrogenation of the palladium catalysts than for the platinum catalysts are often attributed to the formation of conjugated dienes on the catalyst surface (27). Conjugated dienes are known to be precursors in coke formation reactions (28). We therefore suggest a mechanism in which the palladium metal catalyst produces conjugated dienes. We also suggest that these coke precursors cause the deactivation. However, if the conjugated dienes caused the deactivation on the metal sites directly, the palladium on α-alumina would also deactivate. Hence, the role of the carrier is important. Following the formation of the dienes on the metal, polymerization and cyclization would occur on the acid sites of the support (29). The large coke molecules would then be recycled to the metal surface for further dehydrogenation and condensation on the metal surface, causing the loss of activity. Strong adsorption on the metal of larger coke molecules formed on the support could also cause loss of activity. The α-alumina support has a much smaller surface area and is less acidic than γ-alumina, and the polymerization and cyclization reactions on the α-alumina support will not be important compared to the γ-alumina catalysts. For industrial purposes, it is important to consider deactivation by coke formation. Depending on both the metal and the support used for the hydrogenation, catalyst deactivation may or may not be a significant problem. In order to detect activity decay, catalyst studies must be carried out in repeated batch experiments or in continuous systems. For fixed bed reactors, it may be possible to use *in situ* regeneration of the catalyst by oxidation or hydrogenation.

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