Comparison of Two Palladium Catalysts on Different Supports During Hydrogenation

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ABSTRACT: Soybean oil was hydrogenated using two different palladium-based catalysts, 5% palladium on carbon (Pd/C) and 10% palladium on alumina (Pd/A), at various ratios in a 4-L reactor under constant conditions (165°C, 2 bar H_2, and 500 rpm stirring rate). Reaction rate, *trans* isomer formation, selectivity ratios, and melting behaviors of the samples were monitored. Activity of Pd/C was about 10 times higher than that of Pd/A, and the reaction rate showed a strong dependency on the support material. Increases in the concentrations of both Pd catalysts did not have considerable effect on *trans* formation, which is slightly dependent on support material. Oleate selectivity (S_{21}) for all runs varied between 2.48 and 30.34, and type of support material did not have an effect on selectivity. Melting behaviors of the samples were mainly dependent on reaction rates.

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KEY WORDS: Hydrogenation, melting behavior, palladium, reaction rate, selectivity, support material, *trans* isomers.

Industrial hydrogenation of fats and oils is usually catalyzed by nickel catalysts. The use of palladium catalysts is limited by their higher costs. Early reviews showed that palladium catalysts have greater selectivity and activity compared with nickel (1,2).

Ahmad *et al.* (3) reported that catalyst with very high surface area (5% Pd/C) is less active than others at low temperatures, owing to metal deposition within catalyst pores that prevents easy access of molecules. This resistance is decreased at higher temperatures. They also reported that palladium produces more *trans* isomers than nickel at higher temperatures.

Most of papers on the catalysis of oil hydrogenation consider studies based on Pd-catalyzed hydrogenations at lowered temperatures and elevated pressures to obtain less *trans* isomer content. Zajcew (4) hydrogenated a soybean oil/cottonseed oil mixture with 5% Pd/C catalyst at 120°C, under 45 psig H_2 pressure, at a reaction time of 100 min, the hydrogenated sample contained 35% *trans* FA at an iodine value (IV) of 71. Lowering the temperature decreased the *trans* fat content (5). The researcher also tested deactivated Pd/C catalyst for vegetable oil hydrogenation (6).

Hsu *et al.* (7) examined four different Pd catalysts for canola oil hydrogenation at 50 ppm metal concentration, 70 and 90°C, and under 750 psig H_2 pressure. Pd/C was less active despite having the highest surface area. When this catalyst was used at 70°C, the *trans* isomer content of the sample with a 78.5 IV was 13%. The lowest *trans* content at the same conditions was achieved with an alumina-supported Pd catalyst.

Ray (8) hydrogenated soybean oil at three different temperatures (27.6, 60, and 93°C) and pressures (5, 27.5, and 50 psig) using various metal concentrations of 5% Pd/C catalyst. Depending on the conditions, *trans* FA contents of the samples having about 65 IV varied from 38.0 to 57.7%. There was no advantage in using palladium with respect to *trans* formation or selectivity. Berben *et al.* (9) also reported that Pd catalyst did not give any benefits in reducing *trans* fat content when they examined 50 or 65 ppm palladium catalyst at 60°C and 102 psi for hydrogenation of soybean oil.

Low-pressure applications are desired in industry as a matter of economy. Besides, palladium catalysts are much more active but more expensive than nickel-based ones. In practice, this limitation can be minimized by decreasing catalyst ratio at elevated temperatures.

The objective of this study was to compare palladium-based catalysts on two different supports during hydrogenation of soybean oil with respect to the reaction rate, isomer formation, selectivity, and melting behavior of the fat.

MATERIALS AND METHODS

Soybean oil with a FA composition of 10.20% palmitic, 3.77% stearic, 30.70% oleic, 46.44% linoleic, and 8.46% linolenic acid was used in hydrogenation reactions, which were carried out in a 4-L Snap-Tite reactor (Autoclave Eng., Erie, PA) under 2 ± 0.03 bar H_2 pressure, at 500 ± 3 rpm stirring rate and 165 ± 0.5°C. The procedure described by Cizmeci *et al.* (10) was followed for hydrogenation. The two different commercial palladium-based catalysts, 5% palladium on carbon (Pd/C) and 10% palladium on alumina (Pd/A), were purchased from Engelhard (Iselin, NJ) and Aldrich (Diesenhofen, Germany), respectively.

A mixture of 37 FAME (C_4–C_{24}), methyl esters of *cis*-11-vaccenic acid, and a *cis-trans* isomer mixture of linoleic acid were purchased from Supelco (Bellefonte, PA). Methyl esters of *trans*-11-vaccenic acid, *cis*-12-oleic acid, CLA, and *cis-trans* isomers of linolenic acid were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were reagent grade.

The methyl esters of the FA and the isomers were prepared according to IUPAC (11) and analyzed using a Trace 2000 gas chromatograph (Milan, Italy) equipped with an SP 2560 column (100 m × 0.25 mm i.d. × 0.20 µm film thickness) (Supelco).

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Injector, column, and detector temperatures were 230, 175, and 240°C, respectively. Split ratio was 1:100. Carrier gas was helium at 0.7 mL/min ratio.

IV were calculated from FA composition using AOCS Official Method Cd 1c-85 (12).

The solid fact content (SFC) of the sample was measured by low-resolution pulsed NMR using a Maran SFC (Resonance Instrument Ltd., Witney, United Kingdom) according to AOCS Official Method Cd 16b-93 (13). The slip melting point (SMP) was determined in triplicate according to the AOCS Official Methods Cc 3-25 (14).

Reaction rate constants were calculated using a first-order reaction equation,

$$k = \ln (\mathrm{IV}_o / \mathrm{IV}_t)/t \qquad [1]$$

the selectivity ratios were calculated according to a step-by-step saturation scheme,

$$\text{Triene} \xrightarrow{k_3} \text{Diene} \xrightarrow{k_2} \text{Monoene} \xrightarrow{k_1} \text{Saturated} \qquad [2]$$

and the saturation of each component was taken as a first-order reaction. Selectivity ratios were then calculated using a computer program in AOCS Official Method Tz 1b-79 (15) from the following equations:

$$S_{32} = k_3/k_2 \qquad [3]$$

$$S_{21} = k_2/k_1 \qquad [4]$$

RESULTS AND DISCUSSION

Soybean oil was hydrogenated under constant conditions for 100 min with two palladium-based catalysts on different supports (5% Pd on carbon and 10% Pd on alumina). The catalyst concentrations used in the reactions were 2.5, 5, and 10 ppm for Pd/C and 25, 50, and 100 ppm for Pd/A in the oil. During the reactions, the reaction rates, *trans* isomer formation, selectivity ratios, and melting behaviors of the samples were monitored.

As shown in Table 1, at the end of 100 min-reaction time, IV were reduced from 130.1 to 104.0, 78.8, and 61.8 when Pd/C was used at 2.5, 5, and 10 ppm, respectively. Although metal concentrations for alumina-supported catalyst in the reactions were 10 times greater than for carbon-supported catalyst, the IV for 100 min-hydrogenated samples were greater: 109.0, 92.1, and 71.6, respectively. Reduction in IV was similar for the lowest catalyst concentrations (25 ppm for Pd/A and 2.5 ppm for Pd/C) for both catalysts, but using greater catalyst concentrations increased the differences in the IV reductions.

TABLE 1
Iodine Values and Slip Melting Points (°C) of Hydrogenated Samples[a]

	Pd/A					
	25 ppm		50 ppm		100 ppm	
Sample	IV	SMP	IV	SMP	IV	SMP
10	128.7	<15	126.9	<15	125.5	<15
20	126.3	<15	122.5	<15	119.4	<15
30	124.1	<15	119.0	<15	113.7	<15
40	122.0	<15	114.7	<15	106.8	15.6
50	119.6	<15	110.5	<15	100.5	19.8
60	117.8	<15	106.2	16.6	92.8	23.9
70	115.4	<15	102.6	17.7	86.0	26.6
80	112.8	15.2	98.8	21.6	80.7	33.3
90	110.8	15.5	94.8	22.1	75.9	33.8
100	109.0	19.8	92.1	25.6	71.6	37.0

	Pd/C					
	2.5 ppm		5 ppm		10 ppm	
Sample	IV	SMP	IV	SMP	IV	SMP
10	128.8	<15	126.1	<15	122.9	<15
20	127.5	<15	122.3	<15	115.3	<15
30	125.1	<15	116.9	<15	105.6	<15
40	122.5	<15	110.4	<15	97.7	19.0
50	120.2	<15	103.2	15.3	89.9	23.0
60	117.1	<15	97.8	19.4	82.1	29.4
70	113.8	<15	92.0	24.0	76.1	33.5
80	110.3	<15	87.7	28.2	70.6	37.3
90	107.3	15.6	84.3	28.9	65.3	40.2
100	104.0	16.5	78.8	31.7	61.8	40.8

[a] Pd/A, palladium on alumina; PdC, palladium on carbon.

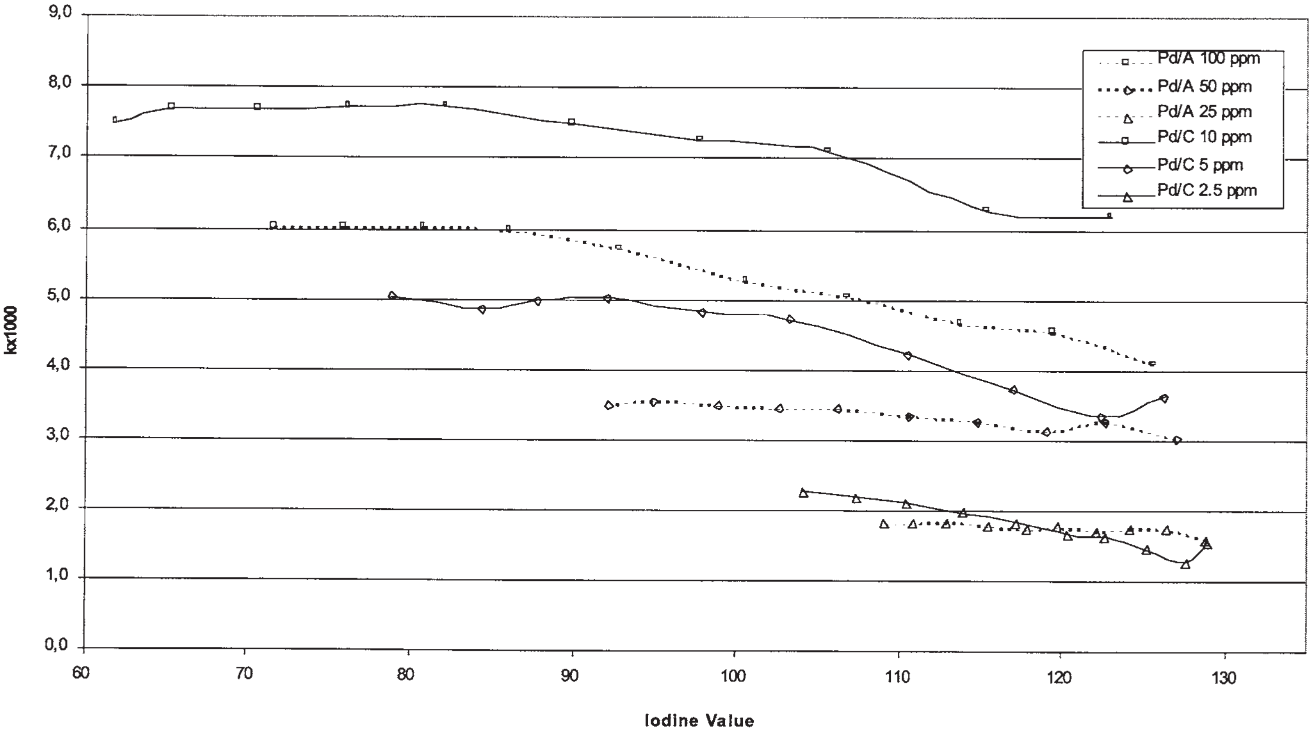

FIG. 1. Changes in reaction rate constant *k* with various dosages of Pd catalysts during hydrogenation. Pd/A, palladium on alumina; Pd/C, palladium on carbon

Figure 1 indicates the effect of catalyst concentration on reaction rate, which increased with greater concentrations of both catalysts but more with Pd/C even though it was used at 10 times greater concentration. That might be due to the higher surface area of carbon-supported Pd (900 m^2/g) than that of alumina-supported Pd (95–115 m^2/g). With the increase of Pd/A concentration from 25 to 50 ppm (2 times), reaction rates increased approximately two fold. However, increasing the active metal concentration of Pd/A from 50 to 100 ppm did not result in the same effect, because the reaction rates increased approximately 1.5 times. Similar behaviors were observed for Pd/C because reaction rates were about 2.5 times higher with the 5 ppm dosage than with the 2.5 ppm, whereas they increased only about 1.65 times when raising the concentration of this catalyst from 5 to 10 ppm.

The concentrations of Pd/C in the reactions were 10 times less than those of Pd/A, and if reaction rates are calculated per unit amount of metal, Pd/C is a much more active catalyst than Pd/A. For example, reaction rate constants of Pd/C and Pd/A at an equal IV (76.1 for Pd/C and 75.9 for Pd/A) were 541.9 and 543.9 min^{-1}, respectively. If they are divided into the metal concentrations (10 and 100 ppm), the *k* values for per ppm of the catalyst are 54.19 and 5.44 min^{-1}. These results suggest that the reaction rate of Pd/C is about 10 times greater than that of Pd/A, which shows a strong dependency of reaction rate on the support material.

The *trans* FA content of the samples is shown in Figure 2. With the lower concentrations of both catalysts (25 and 50 ppm for Pd/A, 2.5 and 5 ppm for Pd/C), nearly identical *trans* isomer contents at equal IV were achieved. But increasing catalyst concentrations from 25 to 50 ppm for Pd/A or 5 to 10 ppm for Pd/C produced little difference in TFA contents of the samples. Hence, the highest TFA content was obtained when IV was lowered to 70.6 by using 10 ppm of Pd/C, while a TFA content of 100 ppm Pd/A was less even though IV was reduced to almost the same point (71.6). It was concluded from these findings that increasing the dosages of both Pd catalysts did not have a substantial effect on *trans* formation although it increased the reaction rates.

In contrast to the reaction rate, *trans* isomer formation is slightly dependent on support material, particularly at low catalyst concentrations, and influenced isomer formation in very narrow ranges. However, Hsu *et al.* (7) found *trans* formation dependent on support material when canola oil was hydrogenated by using 5% of Pd on alumina, carbon, and $BaSO_4$ under 750 psig at 70°C.

Selectivities were calculated according to first-order kinetic equations. Only S_{21} selectivities are presented in Figure 3, because S_{32} selectivities were almost same for all runs and decreased with time due to saturation. For all catalyst concentrations, S_{21} ratios changed between 2.48 and 30.34, and showed an increase as IV reduction increased. Except for the lowest catalyst concentations, S_{21} rates reached a maximum and then decreased owing to saturation. The lowest catalyst concentrations did not give a maximum because IV could not be reduced to a range in which maximal S_{21} ratios were obtained in other

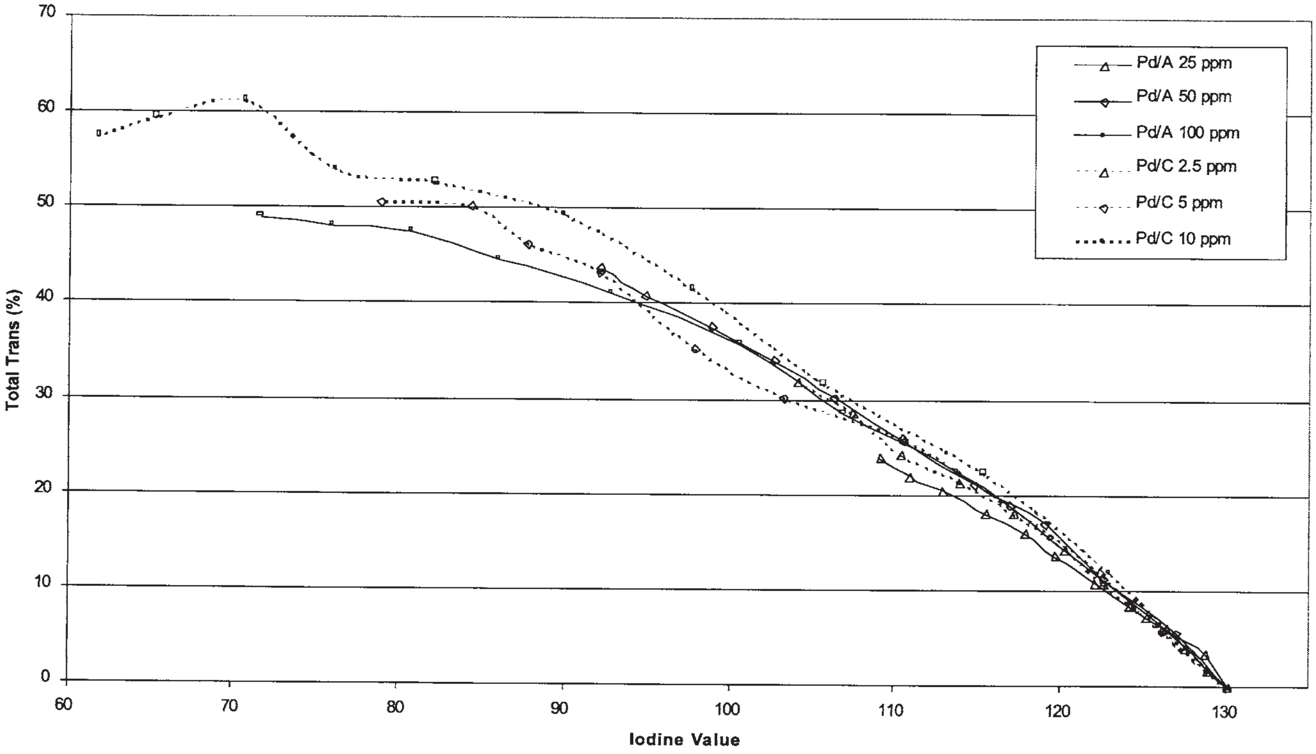

FIG. 2. *Trans* isomer formation vs. iodine value with various dosages of Pd catalysts during hydrogenation. For abbreviations see Figure 1.

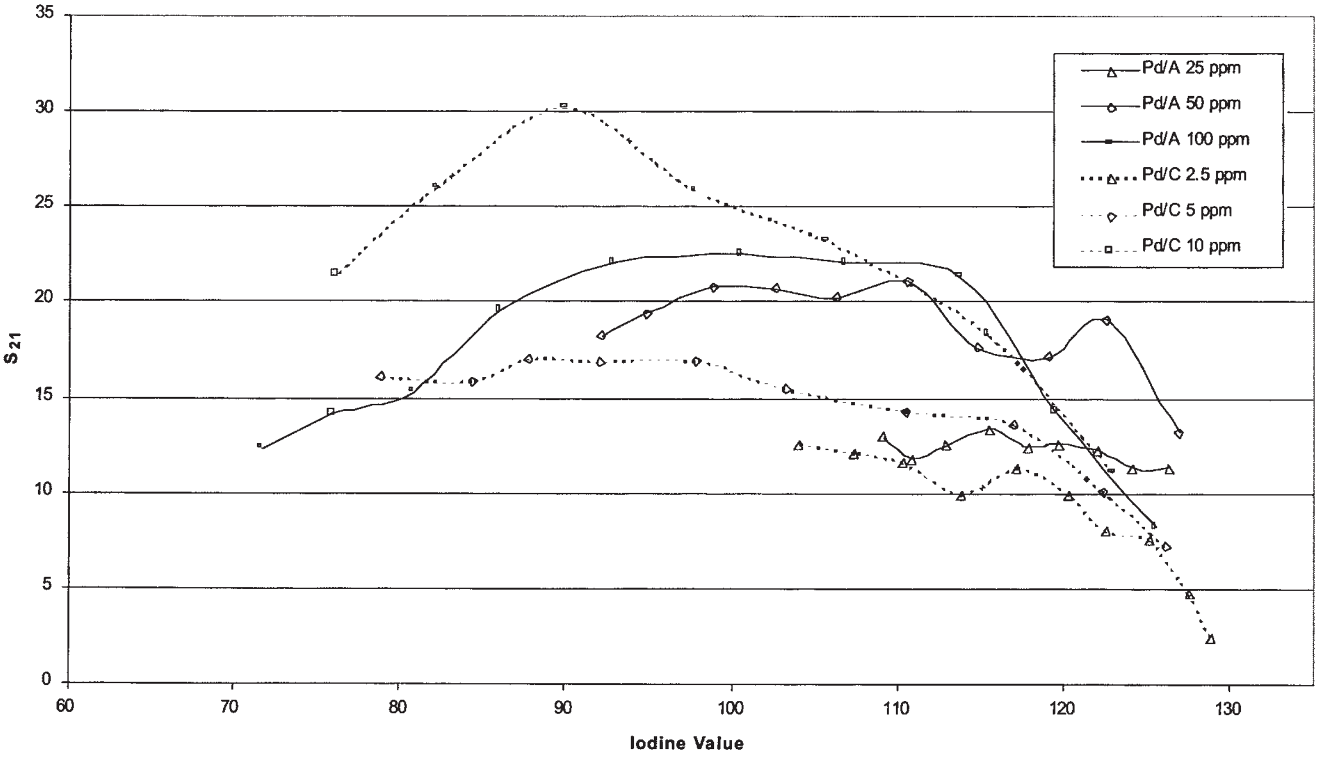

FIG. 3. Changes in selectivity ratio S_{21} during Pd-catalyzed hydrogenation. For abbreviations see Figure 1.

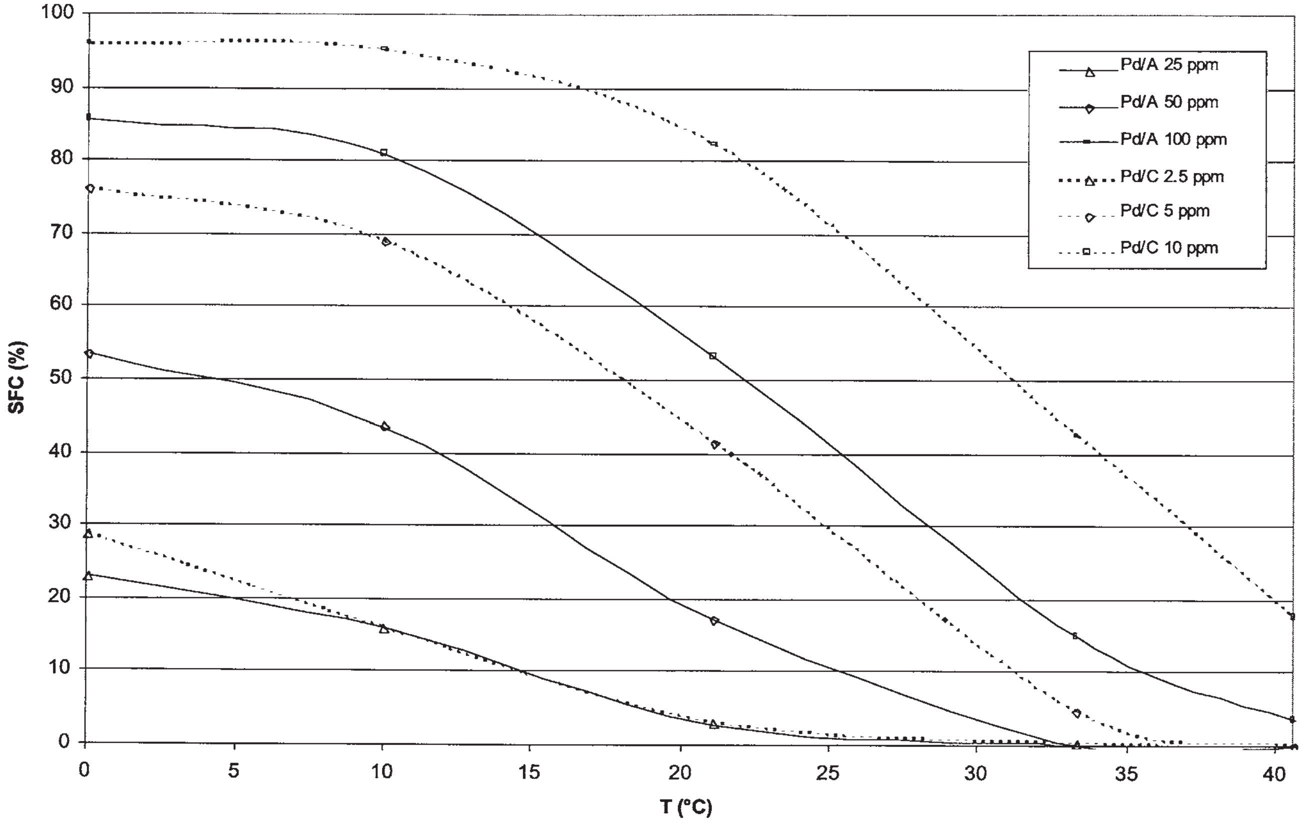

FIG. 4. Solid fat contents (SFC) of samples hydrogenated for 100 min. For abbreviations see Figure 1.

runs. The findings also indicate that 25 and 50 ppm Pd/A are more selective than 2.5 and 5 ppm Pd/C at equal IV, but the selectivity of 100 ppm Pd/A is less than that of 10 ppm Pd/C. For instance, the S_{21} ratio of 25 ppm Pd/A was 12.62 which was higher than S_{21} ratio (9.97) of 2.5 ppm Pd/C when IV were reduced to 119.6 and 120.2, respectively. Similarly, at approximately 98 IV, the S_{21} ratio of 50 ppm Pd/A was higher than that of 5 ppm Pd/C. On the contrary, the S_{21} ratio of 10 ppm Pd/C at 89.9 IV was 30.34, but it was about 22.0 for 100 ppm Pd/A at 90 IV. These results suggest that selectivity is not dependent on support material but mainly catalyst metal type and concentration because of the effect on reaction rate.

Values of SMP of the samples and SFC of the end products are given in Table 1 and Figure 4, respectively. Higher SMP values and SFC were obtained with greater catalyst concentrations owing to higher reaction rates. However, with Pd/C, the reaction rate of hydrogenation was increased and lower IV or more saturation were observed in 100-min hydrogenated samples, which is the reason for higher SFC values of Pd/C. In addition to *trans* formation, similar SMP values were found for the samples of both catalysts at similar IV. These results indicate that, in Pd-catalyzed hydrogenation, reaction rate is the main effect on the melting behaviors of the final product.

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