

The mono *trans* fractions differ in the ratio of the two isomers as shown by capillary GLC (Fig. 7C,7D). Fraction C might have a small amount of *trans,trans* isomer explaining its higher *trans* absorption. The mono *trans* oxidative cleavage shows little difference between the two fractions. The IR absorption for the 9,15 mono *trans* is a little more than that of the elaidate where a 9,12 mono *trans* is ca. 85% of the elaidate (5).

This procedure for preparing 9,15-octadecadienoates is involved due in part to the small percentage of desired product in the starting material and in part to the number of CCD's that have to be performed. The procedure does, however, provide valuable, pure isomers for standardization of GLC and IR analyses.

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Catalysts for Selective Hydrogenation of Soybean Oil.¹

II. Commercial Catalysts

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Abstract

A survey of commercial hydrogenation catalysts demonstrated the higher selectivity ($S_L = 2.4-2.7$) of certain platinum, palladium and rhodium catalysts for hydrogenating linolenic components in soybean oil. Nickel catalysts generally showed selectivities below $S_L = 2.0$ although skeletal nickel achieved higher values. *Trans*-isomers were in the range 7.8-15.4% for the above noble metal catalysts. Nickel catalysts provide a lesser degree of isomerization, 5.2-7.4% of *trans*-isomers for the most selective catalysts.

Introduction

IN A PREVIOUS publication (1), a method was outlined for determining the selectivity of catalysts for the hydrogenation of linolenic components in soybean oil. In the present paper, various commercial catalysts were secured from several manufacturers and the method was applied. The object of the survey was primarily for orientation purposes. Presumably, many of the catalysts had proved commercially successful for hydrogenation processes and it was felt that selectivity might be inherent in a particular class of such materials. The survey should not be considered as a means of obtaining relative ratings, since time did not permit optimization studies for any particular catalyst. However, it was felt that the broad spectrum of products which could be obtained in this way might afford valuable clues in suggesting improved or new catalysts.

Catalysts were received from: the Baker & Co. Div., Engelhard Industries, Inc., Newark; the Davison Chemical Div., W. R. Grace & Co., Baltimore; Girdler Catalysts, Chemical Products Div., Chemetron Corp., Louisville; Harshaw Chemical Co., Cleveland; and Nikko & Co., Ltd., Tokyo. Source and typical compositions, where known, are given in appropriate tables.

Experimental Procedure

The soybean oil used throughout the work was a

refined bleached product obtained from Swift & Co. The following acid composition applied for most of the work:

Component	Amount, %
Palmitic.....	10.0
Stearic.....	3.0
Oleic.....	27.1
Linoleic.....	54.9
Linolenic.....	5.0
Total.....	100.0

The apparatus, experimental procedure, and evaluation method were previously described (1).

Commercial Platinum Catalysts

Platinum catalysts provided good selectivities as evidenced by the selectivity index S_L in Table IA. The selectivity appears to be somewhat temp dependent, i.e., as the temp was raised, the selectivity generally improved. Concurrent with greater linolenic hydrogenation, the formation of *trans*-isomers also increased. The total hydrogenation rate did not increase appreciably with temp, indicative of a high activation energy, a diffusion-controlled process, or both. Since the selectivity improved with temp, the selective nature of the catalyst would appear to play a dominant role. In these experiments, approximately 50% of the linolenic constituents were hydrogenated with the most effective catalysts; this, in general, was found to be a point beyond which further removal proved quite difficult. Since the linolenic concn was then down to 2.5% under such conditions, the selectivity of the catalyst indeed had to be exceptional to obtain further decreases.

The conen of platinum was 0.025%, based on the oil; the dispersion of this conen on different carriers appeared to have little effect in obtaining selectivity. There is slight evidence that the more dilute metal conen (0.5 and 1%) afford somewhat less *trans*-isomerization.

The inclusion of a small amount of organic acid (approximately 5% conen acetic acid) in one test afforded no significant effects.

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TABLE I
Commercial Noble Metal Catalysts
Platinum—Palladium—Rhodium

Description	Temp C	Rate ^a MM/min	So	Sl	Ln removed %	Trans isomers %
A. PLATINUM						
5%—Carbon (A).....	35	0.28	0.1	0.1	6	0.7
	100	0.51	4.6	1.3	30	8.0
	150	0.70	25.6	1.4	48	13.2
5%—Carbon (B).....	100	0.55	14.8	2.2	44	7.6
	150	0.58	large	2.7	52	12.8
1%—Carbon.....	35	0.062	0.3	0.3	4	0.0
	80	0.26	2.9	2.3	36	3.3
	100	0.39	3.9	2.1	38	5.3
1%—SiO ₂	150	0.95	2.4	2.4	48	10.1
	150	0.62	6.0	2.6	46	7.8
0.5%—Al ₂ O ₃	35	0.18	0.3	0.3	4	0.0
5%—Carbon (B).....	100	0.74	10.5	2.3	46	4.5
	100	0.32	72.4	2.4	48	8.4
HAc added.....	150	0.23	130.0	2.2	44	12.8
B. PALLADIUM						
5%—Carbon.....	35	0.36	4.6	1.1	24	5.7
	35	0.43	5.3	1.0	22	5.7
	100	0.97	40.5	2.5	52	13.8
5%—BaSO ₄	35	0.50	5.1	1.5	34	6.4
	100	1.46	19.5	1.7	42	6.2
1%—SiO ₂	80	0.055	2.4	1.2	22	4.0
	100	0.55	6.0	2.6	46	7.8
0.5%—Al ₂ O ₃	35	0.27	4.5	0.6	14	5.4
	100	1.20	108.0	2.3	52	11.4
0.2%—Carbon.....	35	0.11	4.7	1.7	30	3.8
	80	0.48	9.2	1.3	30	8.6
	150	1.54	83.2	2.9	62	15.4
C. RHODIUM						
5%—Carbon.....	35	0.10	1.3	0.8	12	3.9
	35	0.27	0.8	0.8	12	3.1
	100	0.57	23.8	2.7	50	15.4
0.5%—Al ₂ O ₃	35	0.23	1.4	0.7	14	5.3
	100	0.86	330.0	2.6	54	13.8

^a MM = Millimoles.

Commercial Palladium Catalysts

Various palladium catalysts (Table IB) were found to have high selectivities. In contrast to the platinum catalysts, the total hydrogenation rates were markedly influenced by temp. Palladium is an extremely active hydrogenation catalyst and this factor in combination with some intrinsic selectivity characteristics leads to high selectivity and high rate at the max temp investigated (150C).

The formation of *trans*-isomers appeared to increase with increased metal concn on the carrier. The use of barium sulfate as a carrier suppressed isomerization without appreciably affecting activity or selectivity.

These observations appear to be in general accord with the more extended studies of Zajcew (2,3). However, with elevated pressure, Zajcew was able to use palladium concn appreciably below the 0.025% of the current study. According to the above author, palladium catalysts at low hydrogen concn tend to produce *trans*-isomers in greater proportions. This condition would be intensified under atmospheric pressure conditions, as used in the present work. Deactivated palladium catalyst (4) would appear to have merit in deriving selectivity.

Rhodium Catalysts

Rhodium catalysts afforded selectivity as the temp was raised to 100C (Table IC). However, the formation of *trans*-isomers was fairly high under these conditions. As with platinum, the activity of rhodium catalysts did not respond appreciably to temp.

Nickel Catalysts

The performance of nickel catalysts is of interest because of its practical value. The results of Table II demonstrate that while nickel catalysts afforded selectivity, they were not as effective as the noble metals, particularly palladium. However, quite striking is the generally lower level of isomerization, even though temp of 150C were often used. The hydrogenation rates obtained with nickel catalysts, particularly at

elevated temp, were comparable with those of the noble metals. The nickel concn generally used was 1.3% by wt of the oil.

A common form of commercial nickel catalyst comprises nickel-kieselguhr (K) compositions which are prerduced by the manufacturers and stored under hardened oil or tallow. Results of experiments with this form of nickel catalyst show in Table II. The selectivities of all preparations were quite similar. With the 63%Ni-K composition, more experiments were performed than with others. With catalysts of this type, there is an opt temp for selectivity; and it occurred at 100C for this catalyst. This might be a useful factor in practical application since the isomer formation, although low, increases with temp.

Results obtained with various supporting agents for nickel also show in Table II. No particular inferences can be drawn since the nature of these catalysts is not generally available. However, the performance of these catalysts was similar to that of other commercial catalysts containing kieselguhr or other added ingredients.

The unsupported catalysts afforded widely varying results. The 50% solids catalysts is of the Raney type. The relatively high selectivity obtained at 50C in one experiment may be compared with results obtained at 150C in other experiments shown. This difference is directly relatable to the mode of removal of the aqueous medium used to protect the catalyst from air. In the particular experiment cited, a small amount of ethanol was allowed to remain in the catalyst after dehydration. The removal of such ethanol in the course of experimental hydrogenation apparently allowed somewhat improved access of the oil to active catalyst sites at low temp. This result appears related to effects described by Smith and co-workers in hydrogenation studies with Raney nickel catalysts (5,6,7). Such catalysts were found to possess capillaries or pores which affect the kinetics of hydrogenation. If added materials assist entry of reactants to the catalyst sites, the rates of reaction are im-

TABLE II
 Commercial Nickel Catalysts

Description	Temp C	Rate ^a MM/min	So	SL	Ln removed %	Trans isomers %
Kieselguhr-supported catalysts						
25% Ni-10% K.....	150	0.59	7.5	1.7	36	7.9
63.5% Ni-K.....	35	0.17	2.8	1.4	24	2.0
	65	0.52	14.2	1.9	38	5.3
	100	1.06	19.7	2.0	42	5.6
	150	2.33	4.3	0.8	30	8.6
48.5% Ni-K.....	35	0.17	2.4	1.2	22	2.5
25% Ni-10% K.....	100	0.21	2.9	1.1	22	3.6
59% Ni-K.....	80	0.26	4.5	1.8	36	3.4
30% Ni-10% K.....	150	0.81	57.5	1.8	42	5.6
	150	0.96	15.2	1.6	38	6.5
Ni-K.....	65	0.32	1.8	0.2	4	4.8
Ni-K.....	100	0.70	26.1	2.2	42	5.2
Supported catalysts						
Ni-Cu-Mn.....	110	0.35	9.0	1.6	34	3.4
14% Ni-SiO ₂ -Al ₂ O ₃	35	0.45	20.1	1.9	36	5.1
	80	0.50	7.7	1.9	36	4.1
	150	1.59	41.8	1.5	38	7.4
Unsupported catalysts						
27% Ni-flakes.....	150	0.53	15.6	1.6	40	6.2
50% Solids.....	35	0.15	<1.0	<1.0	2	4.7
	50	0.29	14.2	2.5	48	6.5
	65	0.32	<1.0	<1.0	0	4.2
	80	0.47	1.4	0.8	14	6.0
	80	0.21	2.8	0.7	36	6.5
	150	1.34	18.5	2.1	50	5.7
50% Solids.....	150	1.62	50.0	2.2	50	7.4
plus 1% Pt.....	150	0.84	8.0	1.5	28	8.5
plus 2% Pt.....	150	0.27	13.9	1.3	28	6.6
Stabilized Ni.....	150	0.030	1.5	0.3	8	8.7
	150	1.23	12.0	1.4	32	8.8
	80	0.43	3.5	1.4	26	4.8
	100	0.16	7.2	1.8	36	4.7

^a MM = Millimoles.

proved. In the present work, the intrinsic activity of nickel could be achieved at low temp with resultant improved selectivity. While these effects are important, it would seem difficult to obtain consistent results in practical application.

A series of stabilized nickel hydrogenation catalysts has been developed by Yamanaka and his associates (8,9,10). These so-called KSY catalysts have been stabilized with carbon dioxide to render them non-pyrophoric while retaining activity for extended periods of time. These catalysts were found to perform similarly to other commercial products.

Platinum-Promoted Nickel Catalysts

The use of platinum as a promoter to speed the hydrogenation of nitro- and keto-functional groups was reported in 1936 by Lieber and Smith (11) and by Delepine and Horeau (12). The effect has since been confirmed by many workers (13). Although activation appears to be specific for double bonds other than the C=C double bond, it was deemed worthy of study to evaluate the possible selective effect in the current application. In the experiments performed and shown in Table II (unsupported nickel catalysts), some 1 or 2% added platinum provided a specific depressing influence and no apparent selec-

tivity effect. The platinum was added as the preformed salt, (Et₃NH)₂PtCl₆ (14).

Selective Catalysts

The most selective hydrogenation catalysts are grouped in Table III according to their selectivity index, S_L. This tabulation shows that the index is a useful criterion since formation of linoleic component, Lo, or oleic component, O, is also evaluated along with disappearance of linolenic component, Ln.

The noble metal catalysts afforded the highest selectivities. Concurrent with this high selectivity, an appreciable formation of *trans*-isomers occurred. The somewhat lower formation of isomers with silica-supported catalysts suggest that this type of support be studied in greater detail.

Nickel catalysts, according to the selectivity criterion, were less effective in general than the noble metals. Further, unsupported nickel catalysts may have the ability to outperform supported catalysts. However, the activity of such catalysts is known to be uncertain and difficult to use in practical application. A most attractive feature of the nickel catalysts is their low isomerizations. If means can be found to enhance the selectivity of nickel catalysts, it would appear that nickel catalysts would be preferred over

 TABLE III
 Performance of Selective Commercial Catalysts

Description	Increment, Δ%				S _L	Trans isomers %
	S	O	Lo	Ln		
Platinum catalysts						
5% Pt-carbon.....	+0.0	+12.8	-10.0	-2.6	2.7	12.8
1% Pt-SiO ₂	2.7	9.0	-9.4	-2.3	2.6	7.8
1% Pt-carbon (HAc added).....	0.5	12.4	-10.4	-2.4	2.4	8.4
1% Pt-carbon.....	0.7	12.5	-10.9	-2.4	2.4	10.1
5% Pt-carbon.....	0.8	13.7	-12.1	-2.4	1.4	13.2
Palladium catalysts						
0.2% Pd-carbon.....	+0.3	+15.4	-12.6	-3.1	2.9	15.4
1% Pd-SiO ₂	2.7	9.0	-9.4	-2.3	2.6	7.8
5% Pd-carbon.....	0.5	13.4	-11.4	-2.6	2.5	13.8
Rhodium catalysts						
5% Rh-carbon.....	+0.8	+12.0	-10.2	-2.5	2.7	15.4
0.5% Rh-Al ₂ O ₃	0.1	14.3	-11.6	-2.7	2.6	13.8
Nickel catalysts						
Unsupported Ni.....	+1.2	+11.3	-10.1	-2.4	2.5	6.5
Unsupported Ni.....	0.4	14.7	-12.5	-2.5	2.2	7.4
Ni-kieselguhr.....	0.5	11.6	-10.0	-2.1	2.2	5.2
Unsupported Ni.....	1.1	12.4	-13.2	-2.5	2.1	5.7
Ni-kieselguhr.....	0.7	12.4	-10.9	-2.1	2.0	5.6

the noble metal catalysts for this reason as well as cost.

These results are at some variance with those of Johnston et al. (15), who found that the selectivity for several commercial platinum catalysts was significantly lower than for palladium catalysts and below seven out of eight nickel catalysts evaluated. However, elevated temp (80–150C) in the present work provided high selectivities for the noble metal catalysts whereas low selectivities were obtained at 35C. In the cited investigation, the noble metal catalysts were evaluated only at 25C. Also the differences may be related to the relative rates of hydrogenation of the methyl esters and of the glyceride ester mixture. Johnston et al. (15) indicated that the hydrogenation of trilinolenin took four to five times as long as the equimolar mixture of methyl linoleate and linolenate required for their procedure (16).

With nickel catalysts, the cited study and portions of the present work were performed at comparable temp (i.e., 140 and 150C, respectively). However, the high selectivities (1.5–2.7) and the high isomerization (18.0–22.8%) were not duplicated. Thus, radical differences in reaction rates of methyl esters and soybean glyceride mixtures may account for the

anomalous results recorded. Further study is certainly indicated.

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Separation of Triglycerides by Column Chromatography on Silica Impregnated with Silver Nitrate¹

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Abstract

Silicagel impregnated with silver nitrate was used for the column-chromatographic separation of closely related triglycerides. Good results were obtained with 20–100 mg of the following glyceride mixtures:

1. Dipalmito-elaidin and dipalmito-olein.
2. Tristearin, dipalmito-olein, stearo-diolein and triolein.
3. Dipalmito-olein and dipalmito-linolein.

Six well-separated fractions were obtained by chromatography of palm oil and the total triglyceride composition of the oil was calculated from the composition of the fractions.

Introduction

AT THE MOMENT the analysis of glyceride mixtures is being thoroughly investigated. Apart from the fatty acid components, which can be easily determined quantitatively by gas chromatography of the corresponding methyl esters, there is an increasing interest in the way in which the fatty acids are combined with glycerol to form glyceride molecules. The availability of more advanced techniques for the determination of the composition of triglyceride mixtures would indeed contribute considerably to our fundamental knowledge of interesting and highly important subjects, such as the metabolism of triglycerides in mammals and the relationship between the

triglyceride structure and the consistency and rheology of dietary fats.

In earlier publications (1,2) a new chromatographic adsorbent was described for the separation of higher fatty acid methyl esters according to their degree of unsaturation or according to the configuration (*cis* or *trans*) of their double bonds. The adsorbent, which can also be applied to TLC (3,4,5), owes its high selectivity to the presence of a large amount of silver ions. The separation of mg amounts of closely related triglycerides using this type of adsorbent in column chromatography has been briefly communicated (1). The present report gives a detailed description of the results obtained so far.

Experimental

Adsorbent. The preparation of the chromatographic adsorbent (silica impregnated with silver nitrate) has already been described (2).

Solvents. The benzene used was of analytical grade; the diethyl ether distilled before use. The light petroleum was purified from aromates according to the method of Van der Ven et al. (6) and fractionated by distillation. The fraction with a boiling range of 40–60C was used.

Triglycerides. The monoacid triglycerides tristearin (SSS) and triolein (OOO) were prepared by means of the reaction between glycerol and acid chloride (7). The asymmetric triglycerides, dipalmito-elaidin (PPE), dipalmito-olein (PPO) and stearo-diolein (SOO), were prepared from the monoglycerides (8) 1-mono-elaidin, 1-mono-olein and 1-monostearin respectively by acylation in the presence of pyridin and

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