Hydrogenation Catalysts — Their Effect on Selectivity

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ABSTRACT

Catalytic hydrogenation is an important reaction in the processing of fats and oils. During this process, the composition and properties of the lipid mixture are significantly modified. In addition to partial elimination of unsaturation, formation of geometric and positional isomers also occurs, yielding a complex mixture of products. Selectivity is a measure of the tendency for any of these reactions to occur relative to another and is influenced by both reaction conditions and the nature of the catalyst. In this review, the effects of various catalysts on the selectivity of the hydrogenation process are discussed in detail, while only a brief discussion of the effects of reaction conditions is given. The limitations of heterogeneous catalysts such as nickel, copper and platinum-containing catalysts are reviewed with emphasis on recent literature. A similar discussion of homogeneous catalysts such as the soluble coordination complexes of transition metals is also given. While these complex catalysts have been extensively investigated in laboratory studies, they have not been used commercially due to their low activity, high cost, and difficult handling.

INTRODUCTION

Hydrogenation is one of the oldest and most important commercial processes used in the chemical modification of fats and oils. Three incentives for industrial hydrogenation of edible oils have been cited (1):

(a) World production of liquid oils exceeds their consumption, while the supply of naturally occurring solid fats falls short of the demand.

(b) Hydrogenation increases stability against autoxidation, which facilitates distribution to the consumer without loss of quality. In addition, the share of world markets occupied by liquid vegetable oils is increasingly dominated by less stable linolenate – containing soybean and rapeseed oils (2).

(c). Production of soft margarines for refrigerated storage depends on careful hydrogenation and transesterification. Such spreads normally exhibit a high linoleic acid content, as much as 50% of the constituent fatty acids.

In general, hydrogenation is the direct addition of hydrogen across the double bonds of unsaturated fatty acids to convert liquid oils to semisolid plastic fats (3). A consideration of the uses to which hydrogenated fats are put (e.g., manufacture of shortenings and margarine) readily reveals that complete saturation is undesirable. In addition to partial elimination of unsaturation, formation of geometric (2,3,4) and positional isomers (2,3,5,6) also occurs, yielding a complex mixture of products. Selectivity, therefore, defines a means of characterizing a complex system such as this.

DEFINITION OF SELECTIVITY

In the past there has been some ambiguity as to the specific definition of the term selectivity. Mattil (3) stated that hydrogenation is ordinarily selective in the sense that hydrogen tends to add first to the most unsaturated fatty acids. To the fats and oils processors, a selective hydrogenation results in a soft product at a low iodine value or a product of minimum melting point, cloud point or congeal point at a given iodine value (5). Albright (6) defined selectivity as simply the ratio of the reaction rates of the hydrogenation of linoleic acid compared with the hydrogenation of oleic acid. This latter definition has been accepted by the USDA and called selectivity I or S_I (7).

Coenen (2.8) has defined three selectivity concepts, viz, selectivity I, specific isomerization and triglyceride selectivity. Selectivity I describes the degree of preferential hydrogenation of linoleic acid over oleic acid, and is defined as k_2/k_3, where k_2 is the rate constant for the conversion of linoleic to oleic acid, and k_3 represents the rate constant for the transformation of oleic to stearic acid by hydrogenation. High selectivity indicates stepwise conversion of linoleic acid to monounsaturated acids prior to substantial stearic acid formation (2,6,9,10). It should be noted that this type of selectivity may also apply to the hydrogenation of linolenic to oleic acid through linoleic acid (9,10,11). Specific isomerization is an expression of the number of *trans* double bonds formed per double bond eliminated (2). Elevated specific isomerization ratios are indicative of high yields of *trans* isomers. Triglyceride selectivity measures the extent to which the three fatty acid residues in the same triglyceride molecule are hydrogenated independently. Low triglyceride selectivity implies that the hydrogenated product contains a high proportion of tristearin. In addition, Albright et al (12) defined isomerization index as the rate of geometrical isomerization relative to the rate of hydrogenation. High concentrations of *trans* isomers in the hydrogenated fat would elevate this index. Table I summarizes the various concepts of selectivity.

In this paper, hydrogenation literature is reviewed in terms of the type of catalysis and the composition of the catalyst used in the hydrogenation process. Special reference is made to the more recent developments in these areas. A detailed discussion of the factors governing reaction selectivity is not given, as these are discussed adequately elsewhere (2,3,8,9,13,14,15,16,17).

HETEROGENEOUS CATALYSIS

In heterogenous catalysis, which is most commonly utilized in industry, the catalyst and reactants exist in different physical states (3). The catalyst is a solid which is kept suspended in the oil by agitation and on whose surface the hydrogenation reaction occurs. Surface phenomena are therefore of prime importance. Johnson (18) classified catalytic metals according to the orientation and occupancy of the d-orbitals extending above the metal surface:

Class I metals (Mo, W)
Class I metals (Rh, Ir, Ru, Os, Ti, Re)
Class III metals (Fe, Co, Ni, Pd, Pt, Cu, Ag, Au)
Class IV metals (Zn, Ga, Cd, In, Ge, Sn, Pb)

Surface complexes of olefins on metals have been proposed for Class III metals which utilize electrons in the partially filled d-orbitals to form σ-bonds, and for Class II metals which utilize metal itinerant electrons in a delocalized electron bond. There is an expected greater ease of bond formation between olefins and Class III metals over those in Class II, which is considered to be the basis for the greater exchange and isomerization observed during hydrogenation using the former. Consequently, many metal com-

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TABLE I

Several Concepts of Selectivity

Triunsaturated fatty acids $\xrightarrow[k_1]{}$ Diunsaturated fatty acids $\xrightarrow[k_2]{}$ Monounsaturated fatty acids $\xrightarrow[k_3]{}$ Saturated fatty acids

Concept	Definition	Implication of high ratios	Reference
Selectivity I			
Linolenate selectivity	$S_{Ln} = k_1/k_2$	high yield of dienoic acids	2,6,9,10
Linoleate selectivity	$S_{Lo} = k_2/k_3$	high yield of monoenoic acids	9,11
Oleate selectivity	$S_o = k_1/k_3$	high yield of dienoic acids	10
Specific isomerization	Si = No of *trans* double bonds formed No of double bonds eliminated	high yield of *trans* isomers	2
Triglyceride selectivity		Random distribution of fatty acids throughout triglyceride	2
Isomerization index	II = rate of geometrical isomerization rate of hydrogenation	high yield of *trans* isomers	12

TABLE II

Factors Influencing Selectivities in Heterogeneous Catalysis (2)

		Effect on		
Status of dissolved H_2	Increase of	H_2 conc.	S_I[a]	S_i[b]
Increases supply	H_2 pressure	+	-	-
	Rate of agitation	+	-	-
Increases demand	Temperature	-	+	+
	Catalyst concentration	-	+	+
	Catalyst activity	-	+	+
	Unsaturation of oil	-	+	+

[a] Selectivity I.

[b] Specific isomerization.

plexes are known to catalyze the hydrogenation of unsaturated fats, but the major metals are those pertaining to Group III.

In heterogeneous catalysis, those factors which decrease the concentration of hydrogen near the catalyst surface will increase the selectivity I and specific isomerization ratios (2). Table II concisely summarizes these factors. It has been demonstrated that selectivity arises from polyunsaturated fatty acids being more strongly bonded to the catalyst surface that monoenoic acids (19,20). Coenen (2) postulated that either type of acid approaching the catalyst surface will initially be bonded with one double bond. A high concentration of dissolved hydrogen manifests itself in a high coverage of the catalyst surface with adsorbed hydrogen. It was assumed that high hydrogen coverage resulted in rapid hydrogenation of the adsorbed double bonds and low selectivity. Conversely, with low hydrogen coverage, an adsorbed linoleate residue may split off a hydrogen atom from its reactive methylene group and become bonded to the catalyst surface by three carbon atoms. It was proposed that this permits bondings of the second double bond to the catalyst surface and increases the bonding strength of linoleate over that of oleate. Increased selectivity therefore results.

Nickel-containing Catalysts

The instability of the flavor of soybean oil was instrumental in promoting the development of partial (selective) hydrogenation. Since linolenic acid was considered to be an integral part of off-flavor development (21,22), it was felt that selective removal of the linolenate residues might improve flavor stability (10,23). Durkee (24) first patented partial hydrogenation of soybean oil in 1944, and since then numerous developments in the selective hydrogenation of a number of edible oils have been documented. Hydrogenation with nickel catalysts has been the choice of industry, largely due to the availability, low cost and inert nature of the metal to the oil. However, hydrogenation with nickel has well defined limitations (2). Selectivity is never absolute, unless extreme conditions are used, in which case there is a danger of side reactions occurring. Nickel catalysts also have little preference for linolenic acid over linoleic acid. Therefore, in order to reduce the linolenic acid of soybean oil, considerable linoleic acid would also have to be sacrificed in the process. In addition, important amounts of *trans*-acids are formed.

Evans et al (23) selectively hydrogenated commercially refined and bleached soybean oil with 0.2% industrial nickel catalyst at 170 C, 5 psi hydrogen pressure and stirring at 1380 rpm. Hydrogenation with the same catalyst and rate of agitation at 120 C and 100 psi pressure produced nonselective conditions. It should be noted that the linolenate content of both hydrogenated samples was decreased below 2%, and that the stearic acid content of the selectively treated sample did not increase. However, the yield of *trans* isomers was higher in the selectively hydrogenated oil when compared with the nonselectively hydrogenated oil.

TABLE III

Hydrogenation of Soybean Oil with Copper-Chromium Catalysts (52)

Catalyst		Reaction condition A[a]		Reaction condition B[b]	
Name	Composition	Trans %	Linolenate selectivity	Trans %	Linolenate selectivity
G-13	53% CuO, 39% Cr_2O_3	9.2	11.7	---	---
G-22	42% CuO, 40% Cr_2O_3 12% BaO	8.9	12.4	9.0	9.2
T-953	40.1% Cu, 31.6% Cr, 3.7% Cd	6.6	9.5	---	---
T-970	36.6 Cu, 32.7 Cr, 6.7% Mn	8.9	13.0	10.5	6.9
Cu-1106P	40% CuO, 47% Cr_2O_3 10% BaO	8.6	12.2	---	---
Cu-0202P	82% CuO, 17% Cr_2O_3	8.3	10.3	9.5	6.2
Cu-Cr	prepared by urea precipitation	7.5	11.4	9.9	8.7
Cu-Cr	prepared by sodium borohydride reduction	9.3	11.9	8.1	10.0

[a](Catalyst, 1.5 g; oil, 300 ml; temperature, 170 C; pressure 30 psi).
[b](Catalyst 0.3 g; oil, 300 ml; temperature, 200 C, pressure, 30 psi).

Since catalyst reuse is a common practice in the edible oil industry, Albright et al (25) investigated the effect of treating cottonseed oil with new and reused (up to five uses) nickel catalysts at 130-169 C, 45 psi hydrogen pressure and stirred at 1110 rpm. They observed that reuse decreased the linoleate selectivity of the hydrogenation process, especially at lower temperatures. Catalyst activity also decreased after several hydrogenations. It was suggested that this loss of activity allowed a greater concentration of hydrogen at the catalyst surface, which has been shown to decrease selectivity (4, 14, 25, 26). Later studies concerned the hydrogenation of cottonseed oil with 0.1% nickel catalyst (reused plus fresh Rufert catalyst) at 180 C, and 5 to 15 psi hydrogen pressure (27). It was discovered that linoleate was hydrogenated almost exclusively in preference to oleate during the initial stages of the process. Simultaneous and rapid formation of *trans* isomers was also reported. It was postulated that the high selectivity and *trans* isomer formation might be attributed to the formation of conjugated dienes from linoleate at the outset of hydrogenation.

Variations in the type of nickel catalysts used for hydrogenation of vegetable oils have also been studied to some extent. The technique of catalyst preparation, formulation, particle size, pore size and pore size distribution are known to be important in determining the selectivity of the reaction (3, 10, 29, 30). Industrial catalysts are generally metals dispersed in the oxidized state on refractory supports such as clay, kieselguhr or silica-alumina and reduced in situ. The typical catalyst system for the hydrogenation of vegetable oils is usually reduced nickel, dispersed in the absence of air into hardened fat to stabilize it. In such systems the support plays an essential role in determining the specific reactivity of the catalyst (30). This is apparently related to the nickel crystallite size.

The reduction of nickel salts from aqueous or alcoholic solutions with alkali metal borohydrides produces finely divided metal that possesses catalytic activity for hydrogenation reactions (31, 32). This catalyst contained boron in addition to nickel (32). Koritala and Dutton (33) prepared several such catalysts and evaluated their selective hydrogenation characteristics for the linolenyl ester groups in soybean oil. Salts of nickel, cobalt, palladium and platinum gave active catalysts for the selective hydrogenation of soybean oil. Iron and silver salts when reduced with sodium borohydride showed no activity at 200 C and atmospheric hydrogen pressure. Incorporation of palladium, copper, chromium, or platinum up to 2% enhanced the activity of the nickel catalyst.

Stefanovic and Albright (34) also investigated several means by which the selectivity of commercial nickel catalysts might be altered. Treatment of the catalysts with hydrogen sulfide and addition of granular alumina appeared to have no significant effect on selectivity. However, air-dried catalysts tended to increase the selectivity with respect to untreated catalysts when hydrogenation runs were carried out at 170 C.

Hungarian and Russian workers reported high selectivity for Ni-Cu catalysts of varying composition (35-40). It was discovered that the initial stage of hydrogenation of sunflower, soybean and rapeseed oils with Ni-Cu catalyst (containing 20-5% Ni) involved selective conversion of linoleic to oleic acid and intensive formation of *trans* isomers. The second stage involved nonselective hydrogenation and increased production of stearic acid. Conditions for optimum selectivity of nickel catalyst promoted by palladium, platinum, rhodium and ruthenium were also investigated (41,42,43).

Russian researchers (44-47) pioneered work on conjugated hydrogenation, which refers to the hydrogenation process in which hydrogen is supplied by a hydrogen donor rather than being present in the gaseous form (48). Alcohols which are dehydrogenated to carbonyl compounds generally constitute hydrogen donors. Thus, the liberated hydrogen is transferred to the double bond without entering the gaseous phase. Basu and Chakrabarty (48) studied the conjugated hydrogenation of peanut and safflower oils with nickel catalysts and primary or secondary alcohols. They observed that secondary alcohols, as hydrogen donors, decreased linoleate selectivity with respect to primary alcohols. It was also noted that the selectivity depended on the initial unsaturation of the oil when secondary alcohols were utilized (i.e., safflower oil of iodine value 114.4 exhibited greater selectivity than peanut oil of iodine value 93.3). Fukuzimi and Kato (49) investigated conjugated hydrogenation of methyl linoleate isomers and reported higher selectivity with secondary rather than primary alcohols. Chakrabarty et al.(50) studied the nickel-catalyzed conjugated hydrogenation of tung oil, which contains a high proportion of conjugated trienoic acids in the form of eleostearic acid, and concluded that ethanol was more selective than 2-propanol in reducing unsaturated

TABLE IV

Calculated Composition of
Two Hydrogenated Soybean Oils (58)

	Weight, %			
Ester	Original soybean oil	Sample A	Original soybean oil	Sample B
Palmitate	10.0	10.0	10.3	10.3
Stearate	4.2	4.2	4.1	4.1
Oleate	26.0	30.4	22.7	26.7
trans-Monoenoate	---	5.5	---	8.1
Linoleate	52.5	43.2	54.4	40.7
Conj. dienoate	---	0.89	---	3.5
Isolinoleate	---	5.2	---	6.0
Linolenate	7.3	0.7	8.0	0.7

fatty acids.

Copper-containing Catalysts

Due to the fact that linolenic acid has been implicated in the poor storage stability of soybean oil, there has been much interest in developing alternative hydrogenation catalysts which would preferentially reduce the linolenic acid content by selective hydrogenation. In 1963, the first patent utilizing a copper catalyst to selectively reduce the linolenic acid content in soybean oil was issued (51). Since then, much research has been devoted to the development of various copper-containing catalysts and their effect on the selectivity of the hydrogenation reaction.

Koritala and Dutton (52) examined the effects of hydrogenating soybean oil at 30 psi hydrogen, 170 C and 200 C with 0.5% and 0.1% of several types of commercial and laboratory prepared copper-chromium catalysts. Although selective hydrogenation was reported at both temperatures, the lower temperature appeared to be more conducive to greater selectivity. All catalysts reduced the linolenic acid concentration to less than 1% and with selectivity ratios ranging from 6 to 13 (Table III). Linoleate selectivity was reported to be extremely high since little or no stearate formation was observed.

Prompted by these reports of increased linolenate selectivity, Okkerse et al.(53) hydrogenated soybean oil with both copper and nickel catalysts. They reported that soybean oil hydrogenated to a linolenate content of 2%, contained 28% linoleic acid with the nickel catalyst as compared to 49% linoleic acid with a copper catalyst. Using a Cu-Mg-SiO_2 catalyst, a soybean oil containing 1% linolenic acid and 46% linoleic acid was manufactured. High selectivity for linolenate reduction was attributed to the copper portion of the catalyst. These authors pointed out the value of preferential hydrogenation of linolenate in soybean oil to provide flavor stability and to maintain a high concentration of a fatty acid essential to complete human nutrition. It was also noted that the hydrogenated oil should be washed with phosphoric acid (or similar compound) to reduce its copper content to less than 0.1 mg/kg, because copper can act as a prooxidant. Cowan et al.(54) also documented the improved flavor stability of selectivity hydrogenated soybean oil. In general, taste panels assigned superior flavor intensity values to copper-reduced than to nickel-reduced soybean oil.

Koritala (55) examined the activity and selectivity of a number of copper catalysts in the form of copper exchanged molecular sieves, coprecipitated catalysts and supported catalysts. Hydrogenation of soybean oil with these catalysts yielded linolenate selectivities of 4 to 16. Precipitation of copper on Cab-O-Sil, a pure form of silica with a large extenral surface area, produced the catalysts exhibiting the greatest activity and selectivity (55,56).

Popescu et al (57) observed that a catalyst mixture of nickel and copper-chromite possessed suitable activity and linolenate-linoleate selectivities for the production of high oleic (monoene) oils from soybean oil. The hydrogenated product contained 20% dienoic and 66% monoenoic acids. Although their activities were lower, a number of copper catalysts exhibited sufficient selectivity to produce hydrogenated soybean oils of 61 to 72% monoenoic, and 12 to 24% dienoic acid contents. It was also discovered that treatment with citric acid reduced the copper content of the hydrogenated oils to a level comparable to that of the original oil.

Koritala and Dutton (58) determined the composition of soybean oil selectively hydrogenated with copper-chromite catalysts. Argentation countercurrent distribution, column chromatography, infrared spectroscopy, ozonolysis, alkali isomerization and gas chromatography were utilized in the identification of the constituent fatty acids. Based on the data obtained from this study, the composition of the hydrogenation product was calculated (Table IV). Although the double bonds of the *cis*-monoenoic acids were almost exclusively in the 9-position, those of the *trans* monoenes were widely scattered, with the 10- and 11-isomers predominating. The dienoic acids consisted of 86 to 92% linoleate along with minor quantities of *cis, trans* and *trans, trans* conjugated dienes, and dienes with double bonds interrupted by more than one methylene group.

In a subsequent study, Koritala and Scholfield (59) used similar methods to isolate and identify the fatty acid isomers resulting from hydrogenation of methyl linolenate with 10% copper-chromite catalyst at 150 C and atmospheric hydrogen pressure. Extensive isomerization of the double bonds in both the *cis* and *trans* monoenes, as well as the *cis, trans* and *trans, trans* conjugated dienes was reported. The majority of the nonconjugated dienes contained widely separated double bonds. One of the major products consisted of a monoenoic fatty acid containing vinylic unsaturation. Formation of many of these isomers was attributed to conjugation of linolenate as outlined in Figure 1 followed by hydrogenation to form $\Delta^{10,12}$,$\Delta^{11,13}$ and $\Delta^{12,14}$ conjugated dienes. Isomerization, followed by further hydrogenation of these dienes, was proposed to account for formation of the other fatty acids identified in this study. Later work appeared to at least partially confirm this hypothesis (60,61,62). In one of these studies (60), methyl linoleate and several of its isomers were hydrogenated with copper-chromite catalysts. It was discovered that copper-chromite would reduce monoenes, only when the unsaturation was located next to the carboxyl group. In addition, dienes with isolated double bonds were not hydrogenated. It was also observed that esters with conjugated double bonds reacted faster than those with methylene interrupted unsaturation.

Kirschner and Lowrey (63) compared the composition of the products of hydrogenation of trilinolein with copper-

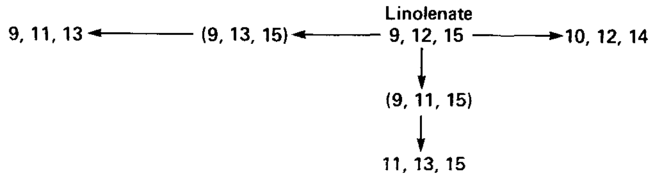

FIG. 1. Isomerization of linolenate during the initial stages of hydrogenation (59).

TABLE V

Performance of Selective Commercial Catalysts (72)

Catalyst composition	Linolenate selectivity	Trans isomers %
Platinum catalysts		
5% Pt-carbon	2.7	12.8
1% Pt-SiO_2	2.6	7.8
1% Pt-carbon (HAc added)	2.4	8.4
1% Pt-carbon	2.4	10.1
1% Pt-carbon	1.4	13.2
Palladium catalysts		
0.2% Pd-carbon	2.9	15.4
1% Pd-SiO_2	2.6	7.8
5% Pd-carbon	2.5	13.8
Rhodium catalysts		
5% Rh-carbon	2.7	15.4
0.5% Rh-Al_2O_3	2.6	13.8
Nickel catalysts		
Unsupported Ni	2.5	6.5
Unsupported Ni	2.2	7.4
Ni-kieselguhr	2.2	5.2
Unsupported Ni	2.1	5.7
Ni-kieselguhr	2.0	5.6

chromite and nickel catalyst. At a comparable iodine value, the copper catalyst produced fewer diene isomers, more monoene (especially *trans*) isomers and essentially no saturates with respect to the nickel catalyst. These results appear to be consistent with previous reports. These investigators also presented evidence in support of the postulate that copper catalysts hydrogenated polyenoic acids by initially forming their conjugated counterparts. It was therefore suggested that the high linoleate selectivity of copper catalysts might be due to the greater ease of conjugation of the triene as compared to the diene.

Pilot plant hydrogenation of soybean oil with several commercial copper-chromite catalysts was carried out under the following conditions: 1% catalyst, 30 psi hydrogen pressure, agitation of 1,400 rpm and a hydrogenation temperature of 170 C (64). The hydrogenated products were found to contain less than 1% linolenate without increasing saturated fatty acid content. It was also observed that heat treatment of one Cu-Cr-Ba catalyst at 350 C in air was necessary for maximum linolenate selectivity.

While copper-chromite catalysts have been the most widely studied, other copper-containing catalysts have been investigated. Koritala (65) reported the preparation of a copper catalyst involving chemisorption of a copper-ammonia complex on a silica gel. Although no loss of catalytic activity was reported following five hydrogenations employing the same catalyst, its linolenate selectivity in conjunction with soybean oil decreased from 18 to 13. Despite this, it was concluded that the catalyst complex was more active and selective than conventionally precipitated catalysts. The same author also prepared a relatively inexpensive coprecipitated copper-silica catalyst of high activity and selectivity (66). Optimum conditions for catalyst preparation included precipitation at 25 to 55 C, freeze-drying and heat treatment at 500 C. The catalyst prepared under these conditions was reported to be more than three times as active as a commercial copper-chromite catalyst. Russian workers recently reported a Cu/$CuSiO_3$ catalyst which possessed greater selectivity in hydrogenating the second double bond in linoleyl groups than Ni-Cu catalysts (67).

Moulton et al (68) hydrogenated soybean oil with copper catalysts containing 1 to 20 parts per thousand of nickel catalyst. The presence of the nickel appeared to cause a slight decrease in linolenate selectivity with respect to straight copper-chromite catalysts. This observation was confirmed by a subsequent plant-scale study (69). This latter investigation also confirmed the feasibility of plant-scale hydrogenation of soybean oil with 0.5 and 0.1% copper-chromite catalyst at 310 F and 30 psi hydrogen. Linolenate selectivities of 5.0 and 5.7 were achieved.

Not only are copper catalysts less active than nickel catalysts, they are also much more sensitive to poisoning, which lowers the selectivity (2). Consequently, reuse is hardly possible, and overall consumption is 5 to 10 times higher than that of nickel catalysts. Koritala (70) investigated the effects of minor components of soybean oil upon the activity of a copper-on-silica catalyst. Trace amounts of free fatty acids, monoglycerides, β-carotene, sodium soaps, phosphoric acid and phosphatides all reduced hydrogenation rates when added to the oil. Squalene, copper soaps, and carbon monoxide had no influence on the activity of the catalyst. However, there was no significant change in either linolenate selectivity or formation of *trans* or conjugated diene isomers when these additives were added to the oil.

Catalysts containing the Platinum Metals

Included in the group of elements known as the platinum metals are ruthenium, rhodium, palladium, osmium, iridium, and platinum (71). These metals have been incorporated into hydrogenation catalysts to varying extents.

Riesz and Weber (72) determined the linolenate selectivity of a number of commercial hydrogenation catalysts containing platinum, palladium, and rhodium. In general, these catalysts showed both greater selectivity and *trans* isomer formation than nickel catalysts during the hydrogenation of soybean oil. The composition, selectivities and *trans* isomer formation of a number of these catalysts are listed in Table V.

Scholfield et al. (73) hydrogenated methyl linolenate at 20 C and atmospheric pressure using a platinum catalyst. The hydrogenation products were isolated and characterized by countercurrent distribution, permanganate-periodate oxidation, alkali isomerization, gas chromatography and infrared spectroscopy. The products of this reaction were compared with those of the hydrogenation of linolenate with a commercial nickel catalyst at 140 C and atmospheric pressure. It was concluded that hydrogenation with platinum is less selective, i.e., more stearate is formed. However, the platinum catalyst appeared to produce less geometric and positional isomerization than the nickel catalyst.

The concept of hydrogenating in the presence of solvents and the use of a selective solvent phase were presented in patent literature (74,75). It was suggested that suspension of the catalyst in the selective solvent layer of a two-phase oil-solvent hydrogenation system might cause preferential reduction of the more unsaturated triglycerides, thereby improving selectivity (74-76). It was assumed that an equilibrium would be maintained between the two phases during hydrogenation, which would cause the more unsaturated triglycerides from the oil to move into the solvent layer, while the more saturated compounds produced in the solvent would tend to migrate back into the oil. Koritala and Dutton (76) increased the linolenate selectivity of 5% palladium-on-alumina catalyst by using dimethylformamide as selective solvent. The elevated linolenate selectivity of dimethylformamide was found to be independent of temperature and catalyst concentration. Furfural, acetonitrile, tetramethylurea and trimethyl phosphate also improved selectivity (Table VI). A recent Russian study (77) was conducted in which soybean and linseed oils containing 11 and 25% linolenic acid, respectively, were hydrogenated in a solution of ethanol at 65 C and under atmospheric pressure, using palladium-on-alumina and nickel-on-support as catalysts. Results indicated that hydrogenation with the nickel catalyst was less selective than with palladium.

Mixtures of methyl linoleate and alkali-conjugated methyl linoleate were hydrogenated with each of nickel, palladium, platinum and copper-chromite catalysts (78). With the exception of platinum, all catalysts reduced conjugated linoleate 10 to 18 times faster than the nonconjugated isomer. Although platinum showed no selectivity at 60 C, conjugated diene reacted four times faster than methyl linoleate in the presence of platinum at 150 C. It was also noted that palladium and platinum reduced conjugated trienes directly to monoenes. Koritala (79) found that the monoenoic products obtained by hydrogenation of alkali-conjugated linoleate with nickel and palladium catalysts were indistinguishable. In general, 44 to 69% of the monoenes consisted of Δ^{10} and Δ^{11} *trans* monoenes, while the Δ^{9} and Δ^{12} *cis* monoenes constituted 20 to 26% of the total profile.

Rylander (80) discussed the industrial applications of noble metal catalysts and concluded that their commercial use was curtailed by economic considerations. Although palladium has been estimated to be from 30 (81) to 80-100 times (82) more active than nickel in hydrogenation of oils, it has not been adapted for large scale partial hydrogenations of natural oils. Because of its activity, very small amounts of palladium are required and as a result, plant equipment must be altered or designed to handle filtration and recovery of small amounts of the catalyst.

Other Catalysts

Although not widely utilized industrially, Mukherjee et al. (83) investigated continuous hydrogenation of soybean oil in a vertical flow-through reactor over a fixed bed of catalyst. Stationary catalysts which were studied included pelleted products containing Raney nickel, reduced nickel, reduced palladium and copper-chromite in addition to Raney-type granulated alloys such as Ni-Cu, Cu-Al, Pd-Al, and Cu-Cr-Al (activated with alkali). Wide spectra of hydrogenation activity, linolenate selectivity and geometrical isomerization were reported. Pelleted copper-chromite and granular Raney copper-chromium exhibited high linolenate selectivity ratios. Pelleted palladium, and granular Raney nickel, copper and palladium were rated as moderately selective. Additional advantages of the hydrogenation system included extremely high rates of reduction and hydrogenated products which are practically free of catalyst particles without filtration.

Recently patented nickel-silver catalysts have been used to hydrogenated soybean oil (84). These catalysts are intended for hydrogenation of highly unsaturated fatty acids in the oil in order to improve flavor and odor. Reports of gold catalysts which produce no discernible isomeric products, and which reduce acetylenic and diene compounds to olefins without saturate formation have also been published (85,86). It was suggested that these catalysts would be especially suitable for hydrogenating natural oils to edible fats.

HOMOGENEOUS CATALYSIS

Homogeneous hydrogenation, stated simply, is that type of reaction in which the catalyst and reactants exist in a single phase (3). In this system, the catalyst functions as individual molecules, which are readily and uniformly distributed throughout the oil. Thus, the structure of the catalyst surface is of negligible importance. It should be noted that homogeneous hydrogenation does not constitute the most extensively utilized system in the edible oil industry.

TABLE VI

Effect of Solvents on Selectivity of 5% Pd-on-Al_2O_3 (76)
(Linseed:Safflower Oil Mixture Hydrogenated)

Solvent	ml solvent/ml oil	Trans %	Linolenate selectivity
None	-	13.0	1.9
Dimethylformamide	3	13.8	3.6
	4	----	3.0
Furfural	2	34.0	3.6
Trimethylphosphate[a]	3	33.0	3.3
Tetramethylurea	2	14.0	3.4
Acetonitrile	4	19.5	3.2

[a] Hydrogenated with a commercial nickel catalyst.

TABLE VII

Production of Simulated Olive Oil from Soybean Oil (92)

Analyses	Hydrogenated soybean oil A	Hydrogenated soybean oil B	Olive oil
Iodine value	95.3	82.0	77-94
Palmitate (%)	10.3	10.2	7-16
Stearate (%)	4.3	4.1	1-3
Other saturates (%)	0.0	0.0	0.1-2
Monoene (%)	60.7	75.7	65-85
Diene (%)	23.9	10.0	4-15
Triene (%)	0.8	0.0	---
Trans acids (%)	6.8	9.5	---

TABLE VIII

Simulated Cocoa Butter from Cottonseed Oil Stearine with Methyl Benzoate – $Cr(CO)_3$ (92)

Analyses	Hydrogenated stearin fractions A	Hydrogenated stearin fractions B	Cocoa butter
Iodine value	38.0	37.8	36.7
Palmitate (%)	58.0	58.9	24.4
Stearate (%)	1.0	1.3	35.4
Monoene (%)	37.6	35.5	38.1
Diene (%)	3.4	4.3	2.1
Trans acids %	7.2	2.5	---
Melting range	30-40	35-40	24-35

Frankel et al. (87,88) reported homogeneous hydrogenation of soybean oil methyl esters with iron pentacarbonyl at 180 C and 310 psi hydrogen. Essentially all of the trienes were reduced, while monoene and stearate concentrations increased significantly. Substantial conjugated diene and *trans* isomer formation were also observed. A subsequent study involved hydrogenation of soybean methyl esters, methyl linoleate and linolenate at 75-180 C and 250-3000 psi hydrogen with 0.2 molar dicobalt octacarbonyl (89). No selectivity for the reduction of linolenate and essentially no hydrogenation of monoenes to saturated compounds was reported.

Complexes of chromium carbonyl, ($Cr(CO)_3$), with methyl benzoate or benzene, effect selective hydrogenation of polyunsaturated fatty acids in vegetable oils and have the added advantage of forming products in which the double bonds are predominantly in the *cis* configuration (90). The all *cis* isomers result in the retention of the liquid state of the oil to quite low temperatures, and this is important in

(i) $MoX_2(CO)_3(Qph_3)_2$ (X = Cl or Br, Q = P or As)

(ii)

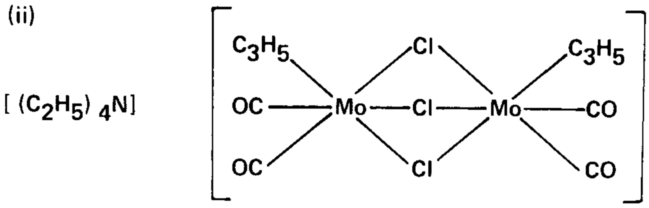

FIG. 2. Postulated mechanism for homogeneous hydrogenation (96).

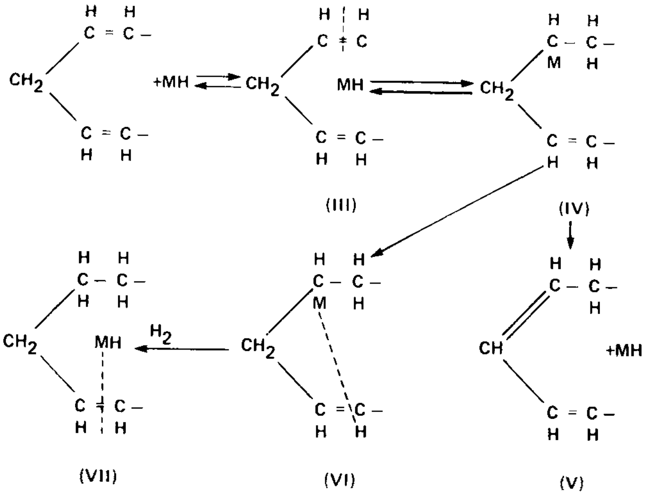

FIG. 3. Structures of two molybdenum catalysts for homogeneous hydrogenation (96).

TABLE IX

[a]Hydrogenation of Soybean Methyl Esters with $Et_4N\ Mo_2\ (CO)_4\ (C_3H_5)_2Cl_3$ (96)

Ester	Original substrate	Final product
Palmitate	11.08	14.08
Stearate	4.8	5.6
Monoene	30.6	47.3
Diene	46.6	31.6
Triene	5.4	0.7

[a]CH_2Cl_2 solvent, 150 C, 500 psi H_2, 5h.

the preparation of liquid salad oils which must avoid cloudiness at low temperature (91). Frankel et al. (92) also utilized the stereoselectivity of chromium tricarbonyl catalysts to prepare synthetic fats, synthetic olive oil from either soybean or safflower oil, and a cocoa butter replacer from cottonseed oil stearines. (Tables VII and VIII).

Ben-Et et al. (93) introduced a two-step approach to the selective hydrogenation of unsaturated fatty acids. The first step involved selective conjugation of the double bonds, catalyzed by potassium *t*-butoxide. The second step consisted of hydrogenation using a catalyst which is specific for conjugated systems such as phenanthrene chromium tricarbonyl. In general, this process yielded high oleic acid products which are relatively low in dienes and trienes. Essentially no formation of saturates was reported.

The catalytic activity of a mixture of chloroplatinic acid and tin (II) chloride has been known for some time (94). This was further investigated by Bailar and Itatani (95) who hydrogenated soybean oil methyl esters, methyl oleate and methyl linoleate with a mixture of dichloro-bis-triphenylphosphine-platinum (II) and tin (II) chloride in 60% benzene: 40% methanol solvent. Nonconjugated diene and triene contents decreased in the hydroagenated soybean oil, while monoenes, and conjugated *cis, trans* and *trans, trans* dienes increased in comparison to the original oil. Hydrogenation of all substrates examined proceeded only to the monoene stage, i.e., no stearate formation was observed. Some stearate formation occurred when mixtures of tetrachloroplatinum (II) ion or hexachloroplatinum (II) ion and tin (II) chloride were used as hydrogenation catalysts.

Bailar (96) proposed a mechanism for homogeneous hydrogenation with catalysts such as $[Pt(PPh_3)_2(SnCl_3)H]$. The initial step involved formation of a π bond between the catalyst (MH) and one of the double bonds in the unsaturated ester substrate (Figure 2). The complex (III) is rapidly transformed into the σ-bonded compounds, (IV). At this point, any of the three following reactions may occur: (a) regeneration of the original substrate and catalyst molecules by reversal of the above reactions; (b) formation of the catalyst and an isomer (V) of the original substrate; or (c) co-ordination of the metal atom, M, with a properly situated ethylenic group. The resulting compound (VI) is stabilized by ring formation. The σ-metal-to-carbon bond is broken upon hydrogenation to yield compound (VII). In the presence of other double bonds in the substrate chain, the above reactions may be repeated. However, in a substrate containing only one double bond, a structure such as (VI) cannot be formed and hydrogenation ceases. Isolation of some of the platinum-olefin complexes proposed above would appear to support the above mechanism (97).

Similar studies have been carried out for palladium and rhodium complexes. Some palladium complexes containing triphenylphosphine and triphenylarsine have been found to be effective and selective catalysts in the homogeneous hydrogenation of soybean methyl esters (98). Again, the characteristic features of the catalysis included the isomerization of *cis* double bonds to *trans* double bonds, migration of isolated double bonds to form conjugated dienes and selective hydrogenation of polyolefins to mono olefins without hydrogenation of mono olefins. It has also been reported that the amount of double bond isomerization accompanying homogeneous olefin hydrogenations over tris (triphenylphosphine) chlororhodium is markedly influenced both by the duration of hydrogen presaturation and the presence of oxygen in the reaction mixture (99).

Certain molybdenum and tungsten complexes, such as those illustrated in Figure 3, have been found to selectively hydrogenate soybean methyl esters (96). The results of hydrogenating with a molybdenum catalyst are outlined in Table 9. The absence of additional stearate in the product should be noted.

The catalytic properties of copper, iron, cobalt, nickel, and palladium chelates derived from the Schiff's bases of 2,2-dialkyl propylene-1,3-diamine with salicylaldehyde have been reported in a recent publication (100). For the most part, the trienes and dienes of soybean oil were hydrogenated to monoenes with negligible or moderate isomerization and double bond conjugation. Increases in the saturated fatty acid content of the hydrogenated products over the original substrate appeared to be small. Linolenate selectivities of 1.3 to 2.9 were reported for copper chelates, while those for iron and cobalt were 1.84 to 3.9 and 0.6 to 5.2, respectively.

In a recent report, Japanese researchers have presented their findings concerning the selective, conjugated hydrogenation of methyl linoleate using indoline and isopropyl alcohol as hydrogen sources (101). Hydrogenation using a $RuCl_2(PPh_3)_3$/isopropyl alcohol system as catalyst and hydrogen donor, respectively, exhibited high linoleate selectivity with little *trans* isomer formation. Indoline, in combination with $PdCl_2$ or $(NH_4)_2PdCl_4$ also showed high selectivity. Each of the RuCl$_2$ (PPh$_3$)$_3$/isopropyl alcohol, (NH$_4$)$_2$PdCl$_4$/indoline and PdCl$_2$/indoline systems reduced methyl *cis, trans* conjugated octadecadienoate completely and rapidly, but showed essentially no reactivity toward methyl oleate. It was suggested that highly selective reduction of linoleate might result from conjugation of the substrate prior to the actual addition of hydrogen.

Although hydrogenations with homogeneous catalysts have been conducted on a laboratory scale for approximately fifteen years, there has been no practical application due to their high cost, low activity and difficult handling (2). Moreover, Bruner and Bailer (102) also pointed out that commercial application was restricted by the expense of catalyst recovery. The use of polymeric analogs of recognized homogeneous catalysts has been presented as a potential alternative to this problem (103). It was proposed that the limited solubility of the polymer in the oil would facilitate ready recovery of the catalyst while retaining the catalytic activity of the monomer. A polymer containing a diphenylbenzylphosphine functional group combined with PtCl$_2$ or PdCl$_2$ constitutes a heterogeneous catalyst that is analogous to the homogeneous catalysts PtCl$_2$ (PPh$_3$)$_2$ and PdCl$_2$ (PPh$_3$)$_2$. Hydrogenation of soybean oil methyl esters with the former proved highly selective, the products being mono- and dienoic in nature, with limited increase in saturated ester content.

Another alternative method of hydrogenating unsaturated fatty acids is by the use of hydrazine (103-107). In contrast to catalytic hydrogenation, hydrazine reduction of polyunsaturated fatty acids results in essentially no formation of *trans* isomers of migration of double bonds. Fractionation and characterization of the products of hydrazine reduction of linolenic acid showed the presence of three monoene and three diene components (106). Monoenes consisted of the 9, 12, and 15 isomers, while the diene fraction included the 9, 12; 9, 15, and the 12, 15 isomers. Any difference in reactivity of the double bonds was small, although the composition of the monoenoates and dienoates suggested a slightly decreasing reactivity for the double bonds near the carboxyl group. This technique, while useful for laboratory reduction, presently holds little promise for commercial use (91).

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[Received June 13, 1978]