REVIEW

Poisoning of Nickel-Based Catalysts in Fat Hydrogenation

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The influence of various poisoning compounds on the hydrogenation of fat is reviewed. Sulfur-containing compounds, present in both vegetable and marine oils, create serious catalyst deactivation problems. In this paper, the poisoning efffect of sulfur and its role on the reactant adsorption in different hydrogenation reactions are discussed. Several factors affecting the sulfur resistance of the catalyst metal are summarized. Other inhibitors influencing the fat hydrogenation, such as phosphorus compounds, free fatty acids, sodium soaps, chlorophyll, halogen compounds and products of lipid oxidation, are also considered.

KEY WORDS: Deactivation, hydrogenation, marine oils, nickel catalyst, poisoning, sulfur, vegetable oils.

Poisoning of supported metal catalysts by sulfur compounds is a common and important problem in many catalytic processes. Sulfur is the major element that readily forms compounds with metal catalysts. Concentrations as low as 1 ppm of H_2S poison transition-metal catalysts, with order-of-magnitude losses in activity as a result. The catalyst deactivation will lead to a decrease of the performance of the catalytic reactor, requiring replacement or regeneration of the catalyst. Nickel catalysts are widely used in hydrogenations, methanation and steam reforming. This use requires careful removal of sulfur-containing compounds from the feed gas and control of temperature because of the sensitivity of these catalysts to feed impurities and thermal sintering (1). The catalyst's life depends on operating conditions and is often reduced to a few months or weeks because of its deactivation. The strong bonding between sulfur and metal catalysts may make their regeneration impractical, leading to expensive catalyst consumption costs.

According to Zrncevic *et al.* (2) there are four basic mechanisms of catalyst deactivation: (i) poisoning: blocking of the active catalytic metal centers. Two limiting cases, uniform poisoning and shell progressive mechanism, can be considered here. For small catalyst pellets with large pores and for low chemisorption rates of poison, the deactivation will be uniform in the whole catalyst pellet. The diffusion resistance throughout the catalyst pellet is negligible due to the uniform deposit of the poison. On the other hand, for large pellets with narrow pores when the affinity of the poison is high, the poison will deposit preferentially in the pore mouth, slowing down the diffusion of the reactants into the pellet interior. It is expected that real systems are between these two limiting cases. Sulfur poisoning is generally very nonuniform because of the rapid and strong sulfur adsorption on nickel. (ii) Fouling: physical deposition of feed species onto the catalyst surface. This phenomenon will lead to loss of active area of the catalyst because of blockage of the catalytic metal sites and pores. (iii) Sintering: loss of the active catalytic area or the catalyst support area. These are respectively associated with crystal growth in the catalyst and collapse of the support. (iv) Loss of catalytic material: formation of compounds, such as metal carbonyls, oxides, sulfides and halides, will result in the loss of catalytic metal. The above-mentioned factors may alter the electronic or geometric structure of the catalyst.

ADSORBED SULFUR AND ITS EFFECT ON THE REACTANT ADSORPTION

The large binding energies of adsorbed sulfur on metallic catalysts can explain the high poisoning effect of sulfur compounds in different reactions (3). Sulfur coverage depends on the metal–sulfur binding energy and the thermodynamic properties of the surface-adlayer interface. At low coverages, adsorbed sulfur atoms are located on sites with the highest binding energies, and the interactions between adjacent atoms are negligible. On the other hand, at higher coverages, sulfur atoms may be gathered into islands. It appears also that sulfur preferentially chemisorbs at high-coordination sites, such as corner and edge sites. Structure-sensitive reactions catalyzed by these types of sites will thus be selectively poisoned. At low temperatures (below 120°C), the adsorption of sulfur compounds is reversible. Irreversible sulfur coverage varies between 0.4 and 1 sulfur atom per accessible metallic atom for most types of the metal. The regeneration will be difficult at these coverages because of the strong metal–sulfur bond. Depending on the chemical nature of metal and sulfur, a charge transfer of electrons is possible. Large differences in electronic affinities between metal and sulfur will polarize the metal–sulfur bond, while the bond will be more covalent with smaller differences in electronic affinities.

Chemisorption of sulfur on the catalyst depends on the electronic properties of the metal. An electron-acceptor type of sulfur shows enhanced adsorption on metals of low electronic affinities. Irreversible sulfur coverage will increase with decreasing electronic affinities. The electronic properties of supported metals can be changed by the acidic properties of the support and the dispersion of the metal. The electronic affinity will be decreased when the particle size is decreased. On the other hand, metals deposited on highly acidic supports are electron-deficient. The toxic effect of a sulfur compound is related to the free electrons in its valence layer, creating a strong chemisorption bond with the catalyst surface. The poisoning effect of the compound will disappear if the free electrons are themselves involved in the formation of a stable nonpoisoning compound. This can be achieved by chemical treatment, usually oxidation.

Ultraviolet photoelectron spectroscopy studies of the adsorption of hydrogen sulfide on nickel showed that the *3d* and *4s* electrons of nickel were involved in the chemisorption bond with the *3p* electrons of sulfur.

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Investigations with other sulfur compounds (thiophene, thiocycloalkanes, alkylsulfides, thiols, disulfides) showed different behavior. For thiophene, thiocycloalkanes and di-*n*-butylsulfide, the extent of sulfiding was limited to the surface atoms, with a maximum value of one sulfur atom per every four nickel atoms. Disulfides and thiols sulfided the nickel by forming a bulk sulfide, probably Ni_3S_2. The coadsorption of sulfur and other species causes a decrease of the adsorption capacity and a change in the binding energy through geometrical and ligand effects, respectively. In the case of H_2, CO and saturated hydrocarbons, the ligand effect decreases the binding energy. For olefinic compounds of high electronic densities on the double bond, the ligand effect will increase the binding energy.

The poisoning effect of sulfur depends on the actual reaction (reaction conditions, nature of the reactants) and the type of catalyst. The poison–metal bond can modify the properties of the neighboring metal–metal bond, creating a new catalytic surface. The poisoning effect of compounds containing two sulfur atoms is less pronounced than that of a one-sulfur-atom compound with similar length because of its double adsorption and consequent lack of rotation. Sulfur decreases the electronic density of the unpoisoned metallic surface due to its adsorption as an electron acceptor; this will favor the adsorption of the reactants that have the highest donor characteristics. The nature of the unsaturated hydrocarbon may alter the extent of the sulfur poisoning; sulfur coverage and poisoning will decrease with increasing degree of unsaturation. In the hydrogenation of butene, the sulfur poisoning is much less pronounced for isomerization than for hydrogenation; hence, butene is adsorbed even when sulfur is present. The deactivation induced by sulfur in the case of hydrogenation may be explained by the inhibiting effect of sulfur on the hydrogen activation, confirming the decreased binding energy of hydrogen adsorbed on sulfided catalysts. More details on the role of sulfur in hydrogenation reactions can be found elsewhere (3).

Agrawal *et al.* (4) concluded that the electronic properties of nickel were unchanged upon sulfur deactivation and that the primary effect of sulfur poisoning was due to geometric blockage of active centers. There is also experimental evidence suggesting that the loss of activity in methanation is due to sulfur blocking of nickel centers on the surface, rather than to the electronic effects (5).

Aguinaga *et al.* (6) showed that the deactivating effects of various sulfur compounds were similar to that of H_2S. This suggests that H_2S produced by hydrogenolysis of sulfur compounds is the actual sulfiding compound. Bartholomew and Katzer (5) proposed that H_2S dissociates completely on the nickel, even at low temperatures. However, there is fair agreement in the literature when the number of nickel atoms involved per adsorbed sulfur atom is considered. Both three-site and four-site mechanisms have been suggested. The former is reported to be favored at least at high temperatures (400–600°C).

Klostermann and Hobert (7) investigated the effects of 13 different sulfur compounds on silica-supported nickel. They concluded that sulfur compounds are chemisorbed dissociatively, resulting in rupture of the S–H, C–S and S–S bonds. Thermodesorption studies showed that most of the sulfur remains on the catalyst. The sulfur blocked the active sites for the dissociation of CO.

A comparison between the heat of adsorption of H_2S on nickel and the heat of formation of bulk sulfides (5) revealed that surface nickel–sulfur bonds are more stable than the nickel–sulfur bonds in bulk nickel sulfides.

Zrncevic *et al.* (2) studied the thiophene poisoning of $Ni\text{-}SiO_2\text{–}Al_2O_3$ catalysts in benzene hydrogenation. They showed that the strength of thiophene adsorption on nickel decreased with increasing temperature and hydrogen partial pressure.

The effect of adsorbed sulfur upon the adsorption of CO on nickel was reported by Bartholomew and Katzer (5). The experimental conditions and the sulfur coverage considerably affect the adsorption. Also, the performance differs between supported and unsupported nickel when CO adsorption is considered. For supported nickel catalysts treated with H_2S, considerable increase in CO adsorption is observed at −83°C to +25°C and 10–60 kPa. This might be a result of $Ni(CO)_4$ formation, which is catalyzed by sulfur. At room temperature, however, CO adsorption is completely inhibited by sulfur when the CO pressure is under 0.1–0.5 kPa, and the fractional coverage of sulfur is over 0.3. Yet, at high temperatures (200–400°C) and CO pressures of 5–10 kPa [total pressure = 100 kPa, $(H_2/CO) = 3$], adsorption of CO by a completely poisoned Ni/Al_2O_3 catalyst is about 50% of that for an unpoisoned catalyst. Hydrogen adsorption on nickel was reduced by preadsorbed sulfur. The degree of reduction is generally proportional to the amount of preadsorbed sulfur.

Wentrcek *et al.* (1) studied the deactivation of supported nickel catalysts under methanation conditions. They concluded that sulfur poisoning of the supported nickel catalyst is the consequence of two simultaneous effects, displacement of CO adsorbate by sulfur and conversion of reactive surface carbon to the less reactive carbon form.

SULFUR RESISTANCE

The metal–sulfur bond is basically covalent. A modification of the electronic properties of a metal due to the electronic transfer from the metal to the sulfur may alter the deactivation character of the metal. The sulfur poisoning resistance of the catalyst may vary with the degree of reduction of the metal, metal–support interactions, metallic particle size, the acid-base properties of the support and alloying (8).

Arcoya *et al.* (9) studied the deactivation of group VIII metal catalysts by thiophene in ethylbenzene hydrogenation. The order of sulfur resistance was found to be $Pt < Pd < Ni < Rh < Ru$. The electron-donor character of the species and the electronic structure of the metal were considered to be the main factors that accounted for the adsorption strength of both thiophene and ethylbenzene.

Okamoto *et al.* (10) studied the electronic properties of nickel catalysts that were modified by the component elements, boron, phosphorus, aluminum and zinc. The electronic properties of metal catalysts are important for the activity and selectivity of hydrogenation reactions. Modification of nickel catalysts will lead to electron transfers between the nickel metal and the component elements. It was shown that electron-rich nickel metal is more resistant against catalyst poisons.

Duprez and Mendez (11) studied the influence of the degree of reduction on the sulfur resistance of Ni/Al_2O_3 catalyst. The reaction tested was toluene steam reforming at 460°C and atmospheric pressure. It was shown that the presence of an unreduced phase can markedly change the performance of metal catalysts. The selectivity is reported to be especially sensitive to the reduction state of the metal. The degree of reduction can be decreased either by increasing metal loading or by impregnating nickel on $NiO-Al_2O_3$ support that was pre-spinelized at 700°C. The authors concluded that the poison resistance of the catalyst was increased by lowering the degree of reduction. The increased sulfur resistance was probably due to the trapping effects of the unreduced nickel species of the carrier and to electronic interaction between Ni^0 centers of the metallic particles and Ni^{2+} species of the unreduced phase. Another hypothesis concerned the geometric effects resulting from dilution of the nickel surface by the unreduced species of nickel. The presence of Ni^{2+} species on the nickel surface inhibits thiophene conversion.

Loss of activity of a nickel-based catalyst is associated with changes in the surface properties (1). Goodman (12) has studied the chemical modification of nickel catalysts by addition of surface impurities. Catalyst activity, selectivity and poison resistance of the pure metal were markedly affected by modification of its surface chemistry. The effect of preadsorbed electro-negative atoms, Cl, N, S, C and P, upon the adsorption–desorption behavior of H_2 and CO on the Ni(100) surface of a single nickel crystal has been discussed. The author reported a reduction in adsorption rate, adsorption strength and capacity of the surface for H_2 and CO. Deactivation is more pronounced when the electro-negativity of the preadsorbed atoms increases. The dominant effect in poisoning by sulfur was suggested to be electronic in nature. This conclusion was also favored by Goodman and Kiskinova (13). In general, the chemical nature of the impurity, its location and concentration are important factors in these modifications.

The rate of deactivation can be decreased by addition of certain metal promoters, such as MoO_3, to nickel (5). A catalyst containing 10% Ni and 20% Mo on Al_2O_3 showed a catalyst life that was a factor of 3 longer than for a 14% Ni/Al_2O_3 catalyst. Also, the use of certain supports, such as ZrO_2, will affect the poisoning rate of nickel. This is probably a result of metal–support interaction because pure ZrO_2 does not adsorb any sulfur.

Sulfur resistance of the Ni-based catalysts is also affected by the support's nature and the preparation method used. Nickel catalysts prepared by impregnation of silica and silica–alumina showed a weak metal–support interaction that was easily reduced. Here, the poisoning decreased as the particle size of the metal increased (structure-sensitive). On the other hand, catalysts prepared by impregnation of alumina or precipitation–deposition showed a strong metal–support interaction. Here, no correlation was found between the deactivation of nickel and metal particle size. The initial deactivation increased as the reduction degree of the metal increased. The type of carrier had no significant effect in this case (8).

Zrncevic *et al.* (14) investigated the effect of catalyst preparation on thiophene poisoning of Ni/Al_2O_3 catalysts in benzene hydrogenation. This reaction becomes structure-sensitive when thiophene inhibits the reaction. For larger nickel crystallites, the reaction rate was less sensitive to thiophene. The lifetime of the catalyst was affected by its pore structure and increased with higher mass transfer resistance.

Hoyos *et al.* (15) studied sulfur poisoning and regeneration of palladium-based catalysts in dehydrogenation of cyclohexane. The authors observed the same deactivation behavior for both hydrogen sulfide and thiophene. They suggested that thiophene is hydrogenated into the deactivating agent H_2S. The influence of support–metal interaction on sulfur tolerance was also discussed. It was shown that the behavior of Pd on $SiO_2-Al_2O_3$ differs from that of Pd on Al_2O_3. The sulfur resistance of the metal is strongly enhanced when Pd is supported on $SiO_2-Al_2O_3$. According to the authors, the strength of the metal–sulfur bond was decreased due to the electron-deficient character of the metal atoms on the surface for an acidic support. It was also demonstrated that $Pd/SiO_2-Al_2O_3$ totally recovered its catalytic activity after hydrogen treatment at 400°C. The recovered activity was even higher than the initial activity. That phenomenon was explained by the changed reactivity of coke precursor in the presence of adsorbed sulfur and the promoting effect of sulfur by creating some particular sites.

CATALYST POISONS IN VEGETABLE OILS

The poisons for nickel catalysts are mainly present in the oil itself. The catalyst poisons may be components of natural oils or decomposition products. Although most of these poisons are removed during different steps in oil processing, small quantities may remain, leading to a considerable decrease of the hydrogenation performance. Among these impurities are sulfur and phosphorus compounds, free fatty acids, oxidized fatty acids and sodium soaps. The content of these compounds in the oil decreases with successive stages of industrial processing before the hydrogenation step. These stages are degumming, alkali-refining, bleaching and deodorizing. Soaps and free fatty acids are considered to be toxic at higher concentrations. The extent of poisoning depends on reaction conditions and on the type and concentration of poisoning compounds. A high reaction temperature and the presence of water will favor the formation of free fatty acids or other inhibitors due to pyrolytic decomposition. Unsupported catalysts are generally deactivated to a greater extent than supported ones. It has been reported that the induction periods of the catalysts are increased with increasing amounts of inhibitors (16).

The chemical nature of sulfur compounds in canola oil (obtained from rapeseed with low contents of erucic acid and glucosinolates) is not fully verified. They are believed to be the hydrolysis products of glucosinolates of the canola seed. Enzymatic decomposition of glucosinolates during the storage of the canola seed produces isothiocyanates, thiocyanates and sulfates. These compounds may be further decomposed into oxazolidine-2-thione, hydrogen sulfide and several other sulfides. The sulfur compounds generate catalyst deactivation and unpleasant odors in heated oil. Wijesundera and Ackman (17) showed that unrefined canola oil contains low levels of sulfur-containing fatty acids that resist the refining procedures. Concentrations as low as 5 mg sulfur/kg of oil will affect hydrogenation markedly. It has been suggested that poisons like sulfur and phosphorus are strongly adsorbed on the nickel surface *via* electron donation (18). It has also been estimated that one sulfur atom will occupy an area of about two nickel atoms, corresponding to 2.38 m^2 of nickel surface per 1 mg of sulfur present.

Organic sulfur compounds are believed to be more efficient poisons than inorganic sulfur compounds. Sulfur compounds present in rapeseed oil have been divided into volatile, thermolabile and nonvolatile compounds. The volatile compounds are probably the most effective catalyst poisons. Abraham and deMan (19) detected nine volatile sulfur compounds in canola oil. All of these were present in both crude and refined oils. Among these compounds, 3-butenyl isothiocyanate accounted for more than 75% of the total. Aromatic sulfur compounds were detected at relatively low levels. Bleached and deodorized oils contained only 3-butenyl and 2-phenethyl isothiocyanates. The authors concluded that volatile sulfur compounds are the main reason for poisoning of hydrogenation catalysts.

Crude rapeseed oils usually contain 10–50 ppm sulfur. Most of this sulfur, however, is removed by conventional refining processes. Daun and Hougen (20) have found seven sulfur compounds in industrially extracted rapeseed oil. Four of them were identified as 5-vinyl-2-oxazolidinethione and 3-butenyl-, 4-pentenyl- and phenethyl isothiocyanate. These are hydrolysis products from glucosinolates of the seed. All seven compounds were also found in fully refined and deodorized oils, but in smaller amounts.

The low sulfur content of canola oil makes sulfur determination difficult. Abraham and deMan (21) have described a chromatographic method for the determination of total sulfur in canola oil. A common method used for this purpose was the Raney nickel method. According to this method, the organically bound sulfur in nonolefinic hydrocarbon solutions is reduced to sulfide by the nickel–aluminum alloy. Addition of acid produces hydrogen sulfide, which can be measured either by titration with standard mercuric acetate and dithizone as indicator or by colorimetry, but the presence of olefins in the sample may give rise to considerable error. Sulfates and sulfides, which are decomposition products of glucosinolates, are not organically bound. Hence, only a small part of the total sulfur presented in oil will be measured by this method, making it unsuitable for measurement of total sulfur in oils. The authors suggested that sulfur compounds in canola oil may be divided into three fractions: volatile sulfur, Raney nickel sulfur and total sulfur. The volatile sulfur can be measured with a gas-liquid chromatograph with a flame photometric detector. According to the authors, in the determination of total sulfur, the first step is combustion of sulfur to sulfate. Ion chromatography, essentially a high-performance liquid chromatography, has been described as a rapid and sensitive method for determination of total sulfur. This method uses specific stationary and mobile phases that are suitable for the separation of different ions and a conductivity detector.

George and Töregård (22) investigated low-boiling nitrogen- and sulfur-containing compounds in rapeseed oil. These compounds were degradation products of the glucosinolates in the oil. The presence of ten compounds was shown by a gas-liquid chromatograph equipped with nitrogen- and sulfur-selective detectors. The authors found no evidence for the presence of substantial amounts of low-boiling (up to 250°C) nitrogen or sulfur compounds in refined rapeseed oil.

The effects of oil processing, hydrogenation and seed condition on the sulfur content of rapeseed oils were investigated by Daun and Hougen (23). The content at different steps of the industrial processes was determined by desulfurization with Raney nickel. The hydrogen sulfide formed by addition of acid was trapped in NaOH solution and titrated with mercuric acetate with dithizone as indicator. In this method, tetravalent and hexavalent sulfur forms are not reduced. Prepress expelled oils had lower sulfur content than the subsequently extracted oil fractions. A major part of the sulfur could be removed by degumming and alkali-refining (from 17–31 ppm S in the crude oil to 4–9 ppm S in the refined oil). Bleaching with activated clays and deodorization further reduced the sulfur content to less than 1 ppm. The sulfur could also be substantially reduced by use of spent (deactivated) nickel catalysts. The effects of moisture content and heat treatment of seed on the sulfur content were also investigated. The sulfur content of the oil increased with increasing amounts of water for the high-glucosinolate seed. For the low-glucosinolate seed, this increase was much less and almost independent of the amount of water added. It is believed that oil-soluble hydrolysis products from the glucosinolates in the seed give rise to increased sulfur content. The effect of heat treatment of seed was detected only for high-glucosinolate seed. In this case, the heat treatment resulted in a higher sulfur content in the oil. The authors concluded that low-sulfur rapeseed oil can be obtained from low-glucosinolate seed with low moisture content and heat in the extraction process at a slightly lower extraction yield.

Abraham and deMan (24) investigated the possibility of removing the sulfur compounds from canola oil. There are different methods of removing sulfur before hydrogenation. Steam stripping at high temperature and low vacuum during deodorization; alcohol–ammonia treatment are among these methods. It was shown that increasing the deodorization time and temperature resulted in increased removal of sulfur. At high temperatures (>200°C), most of the volatile sulfur was removed in a relatively short time (30 min). Pretreatment of the oil with catalyst was shown to remove catalyst poisons. For degummed oil, 24% of total sulfur, 58% of Raney nickel sulfur and 90% of volatile sulfur could be removed by such a pretreatment. For refined oils, these percentages were 29, 37 and 79%, respectively. For both oils, treatment with bleaching earth removed about 22% of the total sulfur but increased the Raney nickel sulfur. No explanation for this transformation was given, but the removal of volatile sulfur was about 85% in both oils.

Koetsier *et al.* (25) presented a new experimental technique to continuously determine the poisoning effect of dibutyl sulfide in the hydrogenation of soybean oil. In this method, the rate of hydrogen absorption is measured by using a press flow controller. In the presence of sulfur, the turnover numbers were calculated to be a factor of five to eight times lower. The medium-pore catalysts showed the highest turnover numbers.

Drozdowski and Zajac (16) have studied the effect of various catalyst poisons on soybean hydrogenation. Allyl isothiocyanate resulted only in an induction period (30–60 min, depending on the sulfur concentration, 11–34 ppm S), after which the hydrogenation course was unchanged. Generally, increasing the concentration of the poison increased the induction period and decreased catalyst activity. The kinetic curves obtained were characteristic for each catalyst and poison.

deMan *et al.* (26) studied the effect of added isothiocyanate on the hydrogenation of canola oil. Canola oil was hydrogenated with the addition of 1, 3 and 5 mg/kg of sulfur in the form of allyl isothiocyanate under both selective (200°C and 48.3 kPa) and nonselective (160°C and 303.4 kPa) conditions with a commercial Ni catalyst. The effect was more pronounced under the selective conditions, where the hydrogenation was stopped at an iodine value of 88 with 5 mg/kg of sulfur. Under nonselective conditions, increased levels of sulfur resulted in prolonging the reaction, but even with 10 mg/kg of sulfur, the reaction could continue down to an iodine value of 70. It was also shown that the nonselective conditions resulted in higher removal of 18:3 and a faster production of 18:0. Further, the amount of *trans* isomers was affected by the addition of sulfur. For both selective and nonselective conditions, the levels of *trans* isomers were increased when 3 or 5 mg/kg of sulfur were added. These effects were more pronounced under selective conditions. Addition of 1 mg/kg of sulfur had almost no effect on *trans* content. Increased amounts of added sulfur resulted in higher dropping points of the hydrogenated oils. The comparisons were made at similar iodine values. The solid fat content of hydrogenated canola oils was increased with increasing levels of sulfur under both selective and nonselective conditions; the former showed higher solid fat levels. The authors concluded that the effect of sulfur addition is greatly influenced by the hydrogenation conditions. Another finding was that the fraction of sulfur adsorbed by the catalyst increases with decreasing temperature and increasing pressure. Therefore, nonselective conditions will result in higher sulfur levels on the catalysts. However, greater poisoning effects were observed under selective conditions, contradicting the abovementioned finding.

Abraham and deMan (27) have investigated the effect of some isothiocyanates (allyl, heptyl and 2-phenethyl isothiocyanates) on the hydrogenation of canola oil with a nickel catalyst. More than 60% of the sulfur in canola oil was 3-butenyl isothiocyanate. Allyl isothiocyanate was reported to be the most effective catalyst poison, and 2-phenethyl was the least. This observation suggests that not only the amount of sulfur but also the type of sulfur is important in catalyst deactivation. The poisoning ability of small radicals attached to isothiocyanates is believed to be higher than that of large ones. Also the fatty acid composition of the hydrogenated oil is affected by sulfur compounds. An addition of 10 mg sulfur/kg oil as allyl isothiocyanate gave the lowest level of 18:0. This, according to the authors, was due to the lower activity of the poisoned catalyst. The amounts of solid fat in the hydrogenations were increased with increasing levels of sulfur. Allyl and phenethyl isothiocyanate showed the highest and lowest effects, respectively. Another interesting result of this study was the effect of sulfur on the percentage of *trans* fatty acids of the partially hydrogenated oils. Increased amounts of sulfur resulted in higher levels of *trans* fatty acids. Again, allyl isothiocyanate produced most *trans* fatty acids. The authors concluded that the size of the molecule has some effect on the toxicity of the sulfur compounds.

Chandrasekhara Rao *et al.* (28) studied the effect of allyl isothiocyanate (up to 0.1 wt% of the oil) on the hydrogenation of groundnut oil. At a level of 0.005%, it slightly promoted the hydrogenation rate. At this level, the isomerization reaction was accelerated, resulting in faster saturation. At a higher level of allyl isothiocyanate (0.01%), the reaction activity was stopped after a half hour. Thereafter, only isomerization took place, leading to 68% *trans* monoene and 28% saturated acids after 7 h. According to the authors, this was due to the loading of allyl isothiocyanate at the acidic sites of the catalyst. These sites were believed to dissociate the molecular hydrogen into the atomic form. At 0.05% allyl isothiocyanate, only *cis*-*trans* isomerization occurred, while the saturation activity was lost. With 0.1% allyl isothiocyanate, even isomerization was markedly suppressed due to high coverage of allyl isothiocyanate. The authors concluded that some degree of adsorption of the unsaturated fatty acids on the catalyst is necessary for allyl isothiocyanate to promote *cis* to *trans* isomerization.

Mustard contains glucosinolates that will form allyl isothiocyanates upon hydrolysis during oil extraction. Handoo *et al.* (29) investigated the effect of allyl isothiocyanate on the hydrogenation of mustard oil to find the optimum level of sulfur that does not affect the reaction rate. Degumming, alkali refining and bleaching removed up to 25% of the poisoning compounds. The bleached oil contained 0.24% allyl isothiocyanate, which decreased with the progress of deodorization (0.081% after 6 h). It was concluded that the tolerance limit of allyl isothiocyanate in mustard oil is 0.18–0.20%. The experimental results revealed that conversion of linolenic acid to linoleic acid and oleic acid increased with decreased allyl isothiocyanate content. Full conversion of linolenic acid was not observed in any of the cases.

Abraham and deMan (18) have studied the effect of allyl isothiocyanate, which is a volatile decomposition product of glucosinolates, on the hydrogenation of canola oil. Larger amounts of sulfur (20 mg sulfur/kg oil) were reported to nearly stop the reaction. The level of *trans* isomers also increased with increased sulfur content in the oil. Hydrogenated canola oil showed a higher solid fat content when the sulfur level of the samples was low. The fatty acid composition of hydrogenated oil was also altered by the addition of sulfur. Higher levels of 18:0 were detected with samples containing low sulfur levels. Generally, catalysts with higher rates of hydrogenation are less easily poisoned by sulfur than catalysts with lower rates. These experimental observations suggest that the poisoning behavior of sulfur compounds is not a simple blocking of the active centers, but rather a modification of them.

Drozdowski and Zajac (30) investigated the effect of phosphorus and sulfur compounds on the hydrogenation of soybean oil. Two types of nickel catalysts were examined in hydrogenations. The induction period (delay in hydrogen absorption at the start of the reaction) was much longer for sulfur compounds than for phospholipids present in the oil. After the induction period, in the case of the supported catalyst, sulfur showed a stronger inhibitory effect than phospholipids in the first stage of the hydrogenation (increasing hydrogen absorption with time). The picture is reversed at the next stage (constant hydrogen absorption rate). It was concluded that while the reaction rate was considerably affected by the presence of these compounds, the selectivity of the process and the isomerization were not changed significantly.

Rutkowski *et al.* (31) have studied sulfur corrosion of process equipment during processing of rapeseed oil. Corrosive effects of sulfur compounds are favored by higher temperature, presence of steam and air, and acidity of the medium. It was concluded that a major part of the sulfur compounds was removed during the degumming and refining processes. The rest of these compounds was removed by the oil deodorizing process. The rate of corrosion was especially high at the "cooking," extraction and toasting steps. The authors recommended use of special materials for processing equipment to minimize the corrosive effects.

Drozdowski and Zajac (32) have studied the poisoning rate of different nickel catalysts. The inhibitors added were phospholipids, allyl isothiocyanate, free fatty acids, sodium soaps and products of lipid oxidation. The experimental results indicated that the reaction rate decreased immediately when the inhibitors were added into the system. In the case of allyl isothiocyanate, the reaction rate was even completely stopped. It was concluded that the inhibitors were adsorbed at once. Another interesting observation was the acceleration of the reaction rate after the initial strong decrease in most cases. This phenomenon suggested that a deblocking of the active sites of the catalyst took place. A transformation of inhibitor molecules on the catalyst and formation of less toxic compounds that desorb easily from the surface served as explanation for this self-depoisoning behavior of the catalyst. The changes described above are observed when the inhibitors are added into the system during the reaction.

Abraham and deMan (33) studied the effect of chlorophyll on the hydrogenation of canola oil. The presence of chlorophyll is mainly due to freezing before the seed has matured sufficiently. High levels of chlorophyll (20–30 mg/kg) in oil require special treatment to obtain acceptable color values, free fatty acid content and oxidation values. In canola seed, chlorophyll is converted to pheophytins during crushing. Generally, physically refined oils have higher chlorophyll content than alkali-refined and bleached oils. The addition of 1 mg/kg or more chlorophyll leads to catalyst poisoning. Also, higher levels of 18:2 were detected with higher amounts of chlorophyll. On the other hand, solid fat levels and dropping points were generally lowered with increased amounts of chlorophyll. The amounts of *trans* isomers formed during nonselective hydrogenation of canola oil (165°C and hydrogen pressure of 303 kPa) were lower with higher levels of added chlorophyll. Similar results have been reported for vegetable oil hydrogenation in the presence of phosphorus. These findings are in contrast with the effects observed with sulfur. The authors explained them by physical blocking of the active sites of the catalyst by chlorophyll. Chlorophyll occupies the pore entrances on the catalyst, preventing the triglycerides from leaving the pores; this leads to higher saturation in the triglycerides. The low availability of multiple bonds and high hydrogen concentration at the catalyst surface reduce the amount of *trans* isomers. This also explains the higher levels of 18:0 for nonselective hydrogenations.

Raju *et al.* (34) examined the effect of soap (0.025–1.0 wt% of the oil) on the hydrogenation of groundnut oil. *trans* Monoenes are normally formed from both linoleate and *cis* oleate. According to the authors, there were two different types of sites on the catalyst surface, the strongly acidic Lewis sites and the weakly acidic Brönsted sites. The dissociation and isomerization were believed to occur on the Lewis sites and Brönsted sites, respectively. With 0.05% of soap, it was reported that the transformation of *cis* oleate to *trans* monoene was suppressed while that of linoleate was not affected. This showed that linoleate was adsorbed on the catalyst under these conditions. The authors concluded that the presence of soap suppressed the dissociation of hydrogen, lowering the quantity of atomic hydrogen.

Chu and Lin (35) have studied the effects of some impurities on the hydrogenation rate of soybean oil. Oils bleached with activated clay showed higher hydrogenation rates than oils bleached with neutral clay. The reason was that the neutral clay could not efficiently remove phosphorus, oxidations products, Fe and β-carotene, which caused catalyst deactivation. In their experiments, phosphorus compounds and oxidation product of the oil showed the most pronounced reducing effect on the hydrogenation rate. While the increase of free fatty acid and carbonyl values could not be correlated with reduced reaction rates, it was shown that the iron content was well correlated with the hydrogenation rate. β-Carotene was reported to have an inhibitory effect on the hydrogenation rate, although most of it is decomposed during refining, bleaching and deodorization. The authors also studied the effect of storage of refined and bleached oil on the hydrogenation rate. The reduced reaction rate could be correlated with increases in carbonyl, oxidation and acid values during storage.

Pokorny *et al.* (36) investigated the oxidative stability of rapeseed, soybean and sunflowerseed oil. Natural phospholipids inhibited the accumulation of hydroperoxides. The activity of phospholipids was believed to be due to their ability to decompose hydroperoxides. The efficiency order of the phospholipids was ammonium salts > soybean lecithin > rapeseed lecithin.

In the presence of bleaching earth in the reactor, higher reaction rates are observed, compared to oil initially treated with bleaching earth. This has been interpreted in terms of interactions of bleaching earth with the inhibitors and the nickel catalyst, respectively. Drozdowski and Goraj-Moszora (37) have investigated the interaction of bleaching earth with a partially deactivated catalyst. Allyl isothiocyanate, phospholipids and sodium soaps were used as inhibitors. It was shown that there is an optimal amount of bleaching earth that leads to a maximal increase in the hydrogenation rate. Their result clearly indicated that the type of inhibitor has a great influence on the magnitude of the effect of bleaching earth. The most pronounced effect was observed for sodium soaps. The acid character of bleaching earth decomposes soaps into fatty acids, which are less toxic. Allyl isothiocyanate showed the lowest interaction with the adsorbent. The positive effect of bleaching earth was reported to be caused by sorption processes, transformation of inhibitors on the adsorbent and direct interaction with the nickel catalyst. Other explanations were dissociation of hydrogen and the conjugation of ethylene bonds of unsaturated fatty acids on the active surface of silicate. On the other hand, when the amount of bleaching earth is excessive, blocking of the metal surface by the adsorbent will lower the reaction rate. The authors concluded that the efficiency of bleaching earth depends upon the type of inhibitor and catalyst in addition to the time of contact with catalyst inhibitors.

Klimmek (38) has studied the influence of some impurities in fatty acids during hydrogenation with supported nickel catalysts. These impurities were divided into three categories: catalyst poisons such as S, N, P, Cl and As; catalyst inhibitors such as decomposition products, gums, alkali soaps and oxidized fatty acids; and catalyst deactivators such as acids, water and carbon monoxide. Catalyst poisons influence fatty acid hydrogenations most significantly. Compounds containing elements of the groups V, VI and VII, which possess lone electron pairs, are generally effective poisons for nickel catalysts. Sulfur and phosphorus are compounds of this type. The interaction is established by electron donation to the unoccupied d-orbitals of the catalyst metal. All types of nickel catalysts were affected by catalyst poisons, and discrepancies in toxic resistance were caused by variation in quality, *e.g.*, different nickel surface areas. The catalyst inhibitors are adsorbed at the entrances of pores on the catalyst, causing physical blocking of the active sites. Their effect on hydrogenation was not as pronounced as for catalyst poisons in the course of fatty acid hydrogenations. Catalyst deactivators lower the hydrogenation rate because of their reaction with the nickel crystallites.

Raju *et al.* (39) studied the effect of phosphoric acid on the fat hydrogenation reaction. An addition of phosphoric acid (0.033–0.1 wt% of fat) resulted in an acceleration of the rate of saturation of groundnut oil. Generally, it is supposed that hydrogenation involves a dissociation of molecular hydrogen among several other steps. Poisoning of the strongly acidic Lewis sites by soap will suppress this step. The role of added phosphoric acid was to increase hydrogen dissociation. Furthermore, the maximum *trans* acid content (almost entirely *trans* monoene isomers) was reached faster in the presence of phosphoric acid. The distribution of positional isomers in the *trans* monoenes was almost unchanged, indicating that adsorption and desorption of unsaturated fatty species were not affected (occurring on another type of site, the weakly acidic or Brönsted one).

CATALYST POISONS IN MARINE OILS

Catalyst deactivation in hydrogenation of marine oils is considerably faster than in vegetable oils. It is caused mainly by sulfur. Fat-soluble compounds containing bromine, arsenic and selenium are other possible deactivating agents. Generally, the impurity content of the oil is affected by the type of raw source from which the oil is produced.

Lunde (40) studied how selenium, arsenic, phospholipids and the bromine content of the fish oil were changed during different oil-processing steps. The amounts of both selenolipids and phospholipids increased during storage (after 4–6 d). This is because of the deterioration of the raw material during storage. This pattern was not observed in the case of bromine and arsenic. Brominated compounds are distributed among both polar and nonpolar lipids, while arseno-organic compounds are characterized as typical polar lipids. The results also indicated that phospholipids and arseno-organic compounds were removed during alkaline treatment. In the case of bromine and selenium, no effects were observed during alkaline refining and bleaching of the oil. However, during hydrogenation, significant decreases in both selenium and bromine contents were observed. The disappearance of selenium was more pronounced than that of bromine. The authors concluded that both bromine and selenium had deactivating effects on the hydrogenation of marine oil.

Mackerel oil contains substantial amounts of halogen compounds. Mørk and Norgård (41) studied the poisoning effect of various halogen compounds on nickel catalyst. With chlorine-containing compounds, the poisoning pattern indicated a fission of the carbon–chlorine bond, forming HCl, which desorbed from the catalyst surface. No poisoning effect was observed for simple alkyl chlorides, *e.g.*, *n*-butyl chloride, *n*-octyl chloride, *n*-hexadecyl chloride or 1,4-dichlorobutane. The authors suggested that any noticeable adsorption of a chlorine compound is dependent upon an activation of the chlorine atom by another chlorine atom on the same or a neighboring carbon atom. Both bromine and iodine compounds were strong catalyst poisons. The poisoning effect of these compounds was ascribed to a simple adsorption equilibrium. In summary, the toxic effect per mol halogen added increased in the order: Cl < Br < I.

Olsen *et al.* (42,43) have studied the refining and hardening ability of fish oil in the presence of sulfur compounds. The hardening time increased linearly with increasing sulfur content of the oil when the catalyst is in excess. If the catalyst amount was reduced, the hardening time increased exponentially with increasing sulfur content. The investigations showed that the thiolesters (volatile sulfur compounds) could not be removed by refining, giving rise to increased hardening time. It was, however, possible to remove these compounds by deodorization. On the other hand, this step would probably have little effect because only a small fraction of the volatile compounds contains thioesters.

Ottesen (44) studied the bleaching of marine oils with four different types of bleaching earth. The bleaching process reduces the amount of poisoning compounds. In this process, three steps are probably involved at the same time: chemical reaction, chemical adsorption and physical adsorption. The experiments were performed in vacuum at 95°C. The amount of catalyst poison decreased slightly when the bleaching time was increased from 10 to 30 min. A temperature increase from 85 to 110°C had the same effect. Water in the oil lowered the ability of most types of bleaching earth to remove catalyst poisons. The removal of soaps (from the neutralization step) was supposed to occur in three different ways: adsorption of soap by bleaching earth, splitting of the adsorbed soap into free fatty acids by the acid in the bleaching earth and filtration of soap. In this study, the author concluded that the second possibility was the correct one. For soybean oil, the amounts of phosphorus were only slightly decreased after the bleaching process.

Christensen *et al.* (45) have studied headspace fractions of industrial oils produced from North Sea fish. GC–mass spectrometry analysis showed a complex but constant pattern of the total volatile fraction of several fish oils. About 100 different compounds, including 14 sulfur compounds, were identified. The chemical structure of the volatile compounds consisted of sulfides, linear and cyclic di- and polysulfides, and a homologous series of methyl thioesters.

Mørk (46) investigated the influence of some catalyst poisons on the rates and products of the hydrogenation of mackerel and capelin oil. It was concluded that the total catalyst deactivation involved three different poisoning effects: Initial poisoning, probably due to the presence of sulfur and bromine, occurs rapidly, deactivating a certain amount of catalyst independent of catalyst concentration (with 0.009% Ni, the rate was approximately zero). Primary poisoning, occurring within the first few minutes, is a strong effect and stands for a considerable part of the fast rate decrease above iodine values of *ca.* 140. Secondary poisoning is slower and reaches a state of equilibrium after 25–30 min. According to the author, the primary and secondary effects are probably associated with different kinds of poisons.

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