Copper Catalysts in the Selective Hydrogenation of Soybean and Rapeseed Oils: IV. Copper on Silica Gel, Phase Composition and Preparation

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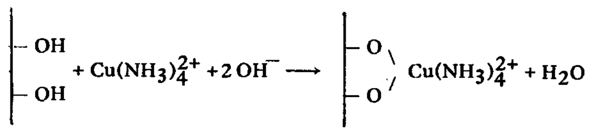
ABSTRACT

Phase composition of a copper on silica gel catalyst was studied with X-ray diffraction analysis. Activity measurements showed three periods of activity, the first two of which were ascribed to a copper surface subjected to reduction and the third one to the reduced form of the catalyst. Hydrogenation reaction over Cu/SiO_2 catalyst has a complex pressure dependence with a rate maximum at 6 atm in the low pressure range. Preparation of the catalyst was studied. On the basis of a proposed reaction model, a catalyst mixture was prepared and tested with good results. In rapeseed oil hydrogenation, Cu/SiO_2 catalysts were shown to be superior to copper chromite catalysts. In soybean oil the two types of catalyst were rather equivalent.

INTRODUCTION

Hydrogenation catalysts based on copper possess high selectivity for hydrogenating the linolenate component of vegetable oils like soybean, linseed and rapeseed oils. Linolenate is reduced 7 to 12 times faster than linoleate. Monoenes are not reduced, therefore the percentage of saturates is scarcely changed during the process of hydrogenation (1,2). Copper is usually charged into the oil as divalent oxidic compounds, which are partly reduced to metal during use. Two active forms of copper have been detected in a study of the copper chromite catalyst performed at this laboratory (3). A mixture of copper metal and copper(I)chromite showed activity mainly during its reduction, while the resulting copper compound, noted as Cu/Cr_2O_3, first became active in a stage of the process where the reduction of the catalyst was completed and water no longer was being generated. Conditions favorable for adsorbing fatty ester molecules exist first of all at the oxidic copper surface, which is possibly activated by a limited reduction to metal (4). The dissociative adsorption of hydrogen is facilitated by copper metal atoms in close contact with adjacent oxide. Thus, judging from earlier work with the copper chromite catalyst, the most ideal copper catalyst, characterized by a constant activity for fat hydrogenation, consists of small copper metal crystallites partially covering a layer of oxidic copper, which is resistant to further reduction. The metallic copper has been formed by reduction of the oxidic phase.

The experiments presented here were carried out in order to construct such a catalyst surface on a support material. Silica gel adsorbs copper ions from ammoniacal solutions in the form of tetrammine complex (5–9). One type of copper ammine polysilicate is formed.



$$\left|\begin{matrix}-OH\\ \\-OH\end{matrix}\right. + Cu(NH_3)_4^{2+} + 2\,OH^- \longrightarrow \left|\begin{matrix}-O\\ \\-O\end{matrix}\right\rangle Cu(NH_3)_4^{2+} + H_2O$$

During washing and activation in air at 300–600 C most of the ammonia is released, and coordinatively unsaturated surface ions of Cu^{2+} are generated (9). The copper adsorbed in this way is more tightly bonded to the gel than in the case of impregnation from neutral solutions. Part of the copper is resistant to complete reduction in hydrogen gas (10).

The method of copper adsorption onto silica gel from ammoniacal solution has been used by Koritala in the preparation of copper catalysts for the hydrogenation of soybean oil (11). A later modified procedure also includes a precipitation step (12), in which the unadsorbed copper ions are precipitated onto the gel by dilution of the adsorption solutions with water. We have tested the catalyst prepared in this way for rapeseed oil hydrogenation and have found that it has a high activity. The method of preparation has been modified for that purpose.

EXPERIMENTAL PROCEDURES

Materials

Hydrogenations were carried out with commercial refined and bleached rapeseed and soybean oils. The different rapeseed oils used in most of the hydrogenation experiments were of medium quality with respect to the erucic acid content (ca. 17%). The oil used in the product evaluation was a "zero-erucic" rapeseed oil, containing only 0.5% erucic acid.

The Cu/SiO_2 catalysts were made from copper(II)-nitrate trihydrate and ammonium hydroxide. The support material was obtained from Davison Chemical Division, W.R. Grace & Co. (MS-Gel 951, specific surface area 600 m^2/g, pore volume 1 cm^3/g, and average pore diameter 67 Å). In addition to the catalysts prepared here, a sample of Cu/SiO_2 catalyst from W.R. Grace & Co., described as "CuO catalyst for vegetable oils hydrogenation" (5.0 wt % CuO, 94.8 wt % SiO_2, specific surface area 250 m^2/g, pore volume 0.79 cm^3/g, and average pore diameter 126 Å) was used. The copper chromite catalyst used for comparison was supplied from Harshaw Chemical Company (Cu-1106P; 40% CuO, 47% Cr_2O_3, and 10% BaO; 40 m^2/g).

Analytical Methods

Analytical methods have been previously described (3). Methyl esters were analyzed with a BDS column. Iodine values were determined according to the Wijs method. The percentage of conjugated dienes in the oil was calculated from the UV absorption at 232 nm. The X-ray diffraction analyses of catalyst samples were performed with a Philips PW 1050/25 diffractometer (Cu-K radiation, 45 kV and 24 mA). The ESCA measurements were performed with an AEI ES10 electron spectrometer. The amount of copper adsorbed at the silica gel was determined by atomic absorption spectroscopy.

Catalyst Preparation

The Cu/SiO_2 catalysts were prepared according to the procedure given by Koritala (12), in which ammonium hydroxide is added to an aqueous solution of $Cu(NO_3)_2$,

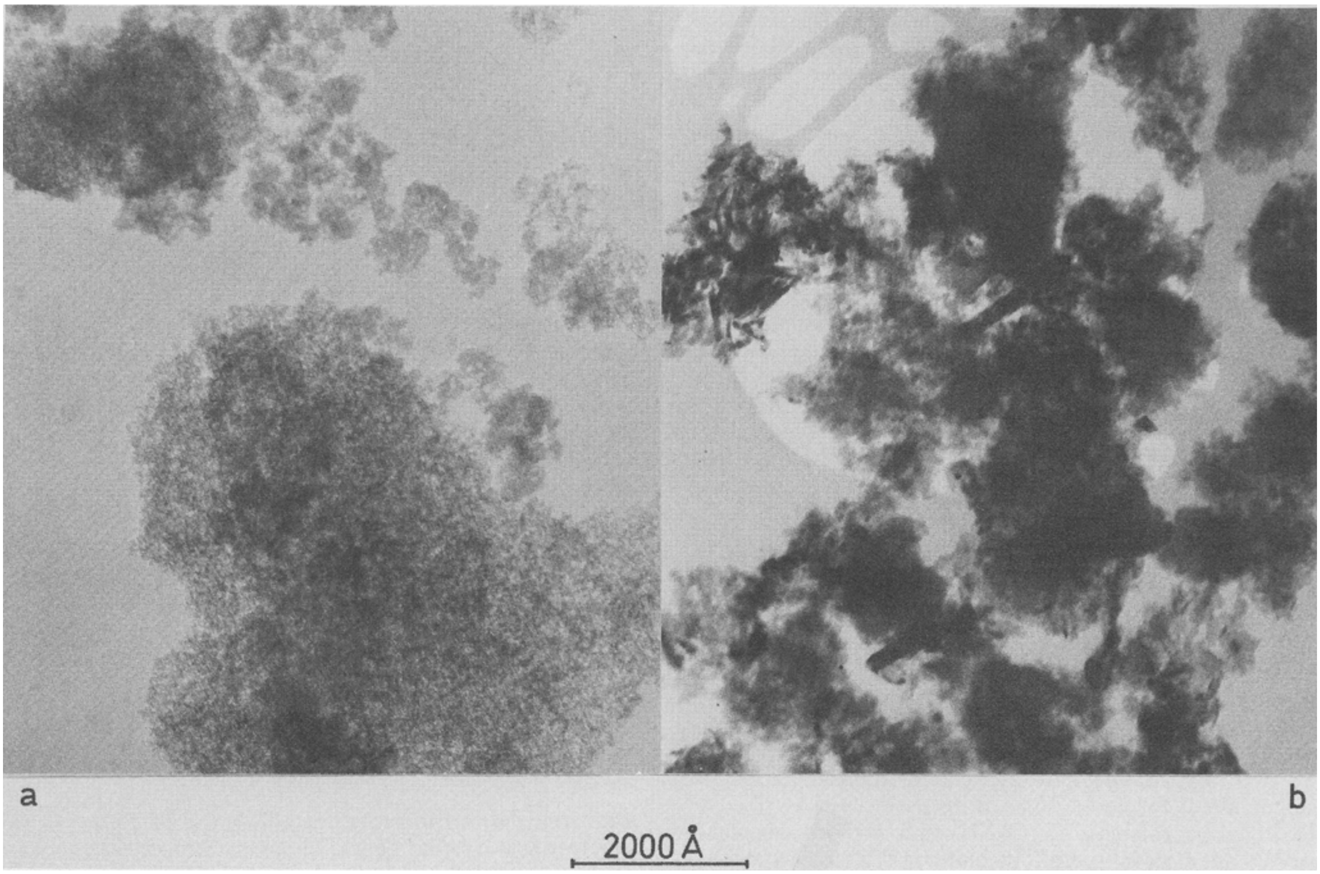


FIG. 1. MS-Gel 951 (a) and Cu/SiO_2 catalyst containing 17% Cu (b).

$3H_2O$. The copper hydroxide precipitate is redissolved. Silica gel is added to the copper solution and part of the blue ions are adsorbed onto the gel. The remainder of the copper ions is precipitated onto the gel as copper hydroxide when the solution is diluted with distilled water. The procedure is repeated once. The pale blue catalyst is dried over night at 110 C and calcined at 350 C for 2 hr.

The composition of the adsorption solution was varied in this study. The catalyst prepared according to the Koritala procedure (12) is prepared from 2 x 25 ml of an aqueous solution containing 2 x 1 g of $Cu(NO_3)_2 \cdot 3H_2O$ and to which 2 x 1.44 ml of a 25% NH_4OH solution has been added. The solutions are diluted to 200 ml and 400 ml, respectively.

Equipment and Operating Procedures

Hydrogenations were carried out in a 1 liter Parr apparatus. The oil to be hydrogenated and the appropriate amount of catalyst were charged into the autoclave. After flushing with nitrogen, the oil and catalyst mixture was heated to reaction temperature while stirring under reduced pressure. The reaction was started by admitting hydrogen into the bomb.

In all the experiments presented here, 300 g oil was hydrogenated at a stirrer rate of 1700 rpm and with a hydrogen flow through the oil of 50 liter/hr, measured after the outlet valve at 1 atm and 20 C. No hydrogen gas was recirculated. The volumetric mass transfer coefficient ka of the gas-liquid interface under the mass transfer conditions in this study has been found to be $ka = 0.65\ sec^{-1}$ (13). The experimental results are considered to be independent of the external mass transfer resistances.

RESULTS

The Phase Composition of the Cu/SiO_2 Catalyst

The phase composition of the Cu/SiO_2 catalyst was studied in experiments with a catalyst sample prepared from $Cu(NO_3)_2 \cdot 3H_2O$ according to the procedure given by Koritala. In this study, that type of supported catalyst contains the highest percentage of copper.

The X-ray diffraction spectrum shows, besides the peak of amorphous silica gel, a broad peak around $35°2\theta$ (d = 2.56Å), which indicates the presence of small CuO crystallites. The electron microscopy pictures show small crystal needles (Fig. 1). The BET surface area of the emerald green material is ca. 350 m^2/g.

The catalyst is reduced during use and water is generated. In soybean oil the color changes from green to grey-black even at 3 atm H_2 pressure. X-ray diffraction analyses showed that crystalline phases of Cu metal and Cu_2O are formed during the first few minutes.

In rapeseed oil at 3 atm H_2 pressure, however, the color variation is limited to a change from emerald to olive-green. Only Cu_2O appears in the X-ray spectra of samples used for 120 min. Catalyst samples used in rapeseed oil hydrogenation with H_2 pressure above 20–25 atm are black and contain, according to X-ray analyses, Cu and Cu_2O. Irrespective of the oil hydrogenated, the black samples change to green when exposed to air at room temperature.

Catalyst samples from rapeseed oil hydrogenation at 3 atm were subjected to ESCA measurements in order to find out if Cu metal is formed in small amounts at the catalyst surface even at low H_2 pressures. No Cu° atoms were detected. Prior to the ESCA work, the catalyst must be subjected to a careful washing procedure in chloroform.

From the change of color it follows that Cu metal of reduced Cu/SiO_2 catalyst is readily re-oxidized. Thus, the result obtained does not exclude the existence of Cu° atoms during the hydrogenation.

From experiments described above it follows that the copper of the Cu/SiO_2 catalyst is more resistant to reduction than that of the copper chromite catalyst, in which 95% of the copper content is reduced to metal.

Changes in Catalyst Activity during Hydrogenation

The activity of the Cu/SiO_2 catalyst as a function of the reaction time was determined as previously described for the copper chromite catalyst (3). A number of identical hydrogenation runs in soybean oil at 3 atm and 185 C and in rapeseed oil at 6 atm and 185 C were interrupted at different reaction times. The catalyst lot of each run was separated from the oil and charged into soybean oil, which was hydrogenated at 6 atm and 185 C. The activity was estimated from the value of $1/t_3$ min^{-1}, where t_3 was the time required for an iodine value drop of 3 units. The activity of the unused catalyst charged directly into original soybean oil was set to 100%.

The activity curve of a Cu/SiO_2 catalyst, prepared according to the procedure given by Koritala, used in soybean oil at 3 atm and 185 C (0.1 wt % in the oil) shows three periods of activity (Fig. 2). The curve is in this respect similar to that obtained with the use of copper chromite catalyst in soybean oil at 3 atm. Regarding that catalyst, the two first periods were ascribed to the two periods of copper metal formation. The third period was ascribed to the reduced catalyst, Cu/Cr_2O_3, the activity of which appears in a stage when the reduction of the catalyst is finished, and the water generated has been removed from the oil. The interferences of the crystalline phases of the Cu/SiO_2 catalyst during the hydrogenation are too small to be used to estimate the copper metal content in the catalyst samples.

The activity of the catalyst used in rapeseed oil at 6 atm H_2 pressure decreases during the first minutes of the process. An increase is observed after about 20 min. Also in this respect, the Cu/SiO_2 catalyst behaves similarly to the copper chromite catalyst (3).

Effect of Hydrogen Pressure on Rate of Reaction

Figure 3 shows the mean rate of reaction $15/t_{15}$, min^{-1}, as a function of the hydrogen pressure p_{H_2}, atm, where t_{15} is the time required for an iodine value drop of 15 units (Cu/SiO_2 with 17% Cu, 0.12 wt % Cu in rapeseed oil).

The complex form of the curve is depending upon changes in the phase composition of the catalyst during reduction from Cu^{II} to Cu^{0}. However, there is also a poisoning effect of water. Rate maximum is obtained at the pressure level of saturated water vapor at the reaction temperature (ca. 11 atm/185 C and ca. 15 atm/200 C). The effect of water results in a higher rate at 12 atm/185 C than at 12 atm/200 C, which is remarkable. The effect of water was earlier observed for the copper chromite catalyst (4). Above the pressure level of saturated water vapor, the rate of water removal is considerably lower and the water generated during the catalyst reduction stays longer on the catalyst surface and within the oil bulk, causing catalyst poisoning.

Cu metal has been detected as a crystalline phase after hydrogenation at H_2 pressures above 20–25 atm (185 C). The mean rate of reaction over the grey-black catalyst surface increases with pressure in the interval studied $20 < p_{H_2} < 30$ according to the equation

$$15/t_{15} = k \cdot (p_{H_2} - 14.5)^{0.5} \qquad 1.$$

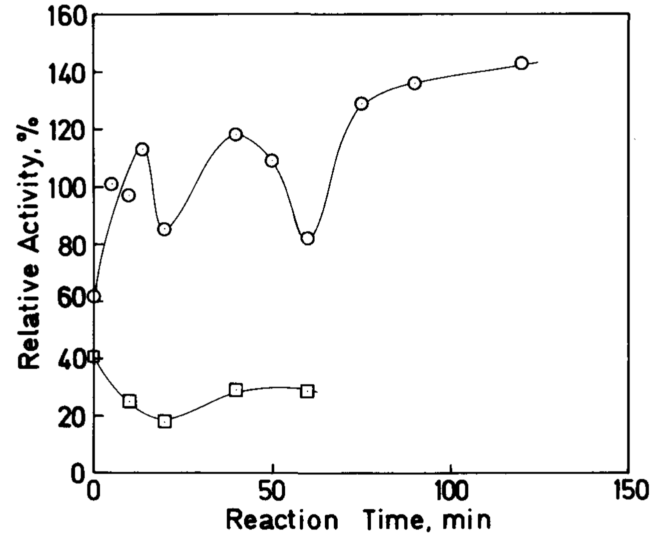


FIG. 2. Relative activity of the Cu/SiO_2 catalyst (17% Cu) after its use in soybean oil at 3 atm/185 C (○) and in rapeseed oil at 6 atm/185 C (□); 0.10 and 0.15 wt % Cu in the oil, respectively.

This equation is like that of Cu-1106P in soybean oil (4), which is valid in the range $13 < p_{H_2} < 20$ (185 C)

$$15/t_{15} = k' \cdot (p_{H_2} - 12.0)^{0.5} \qquad 2.$$

The contribution from the metallic phase of copper to the catalyst activity thus appears at a somewhat higher pressure with the use of the Cu/SiO_2 catalyst.

The hydrogenation performed below 20 atm H_2 pressure proceeds for the most part over an oxidic catalyst surface, i.e., a surface containing monovalent and probably also metallic copper. A maximum rate is obtained at 6 atm.

Effect of Pressure on Selectivity

The selectivity S_{Ln} towards the linolenate component of the rapeseed oil has been calculated from the GLC composition according to the program given by Butterfield et al. (14), using the simplified model of reaction including consecutive first order reactions. The values given in Figure 4 correspond to an iodine value drop of 15 units.

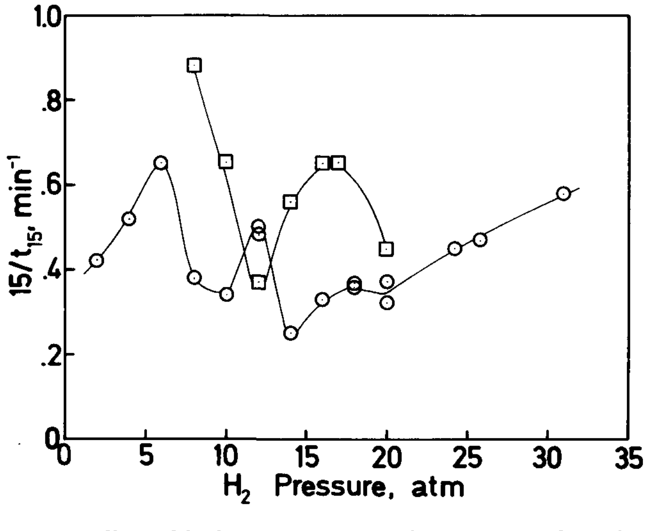


FIG. 3. Effect of hydrogen pressure on the mean rate of reaction in the hydrogenation of rapeseed oil at 185 C (○) and 200 C (□); Cu/SiO_2 (17% Cu) and 0.12 wt % Cu in the oil.

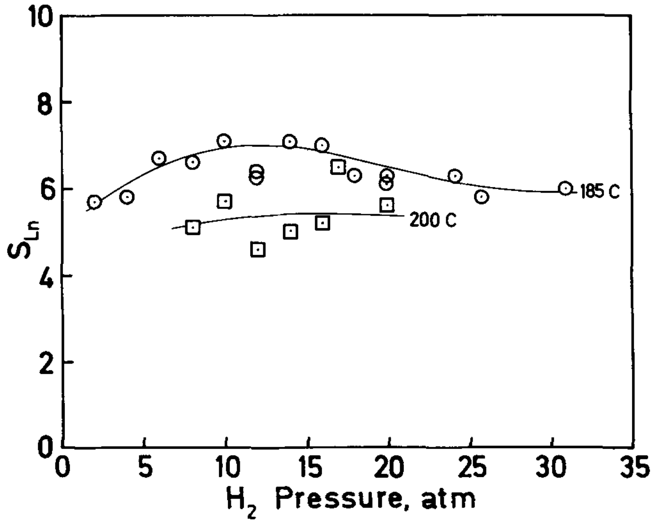


FIG. 4. Effect of hydrogen pressure on the selectivity S_{Ln} at hydrogenation of rapeseed oil; Cu/SiO_2 (17% Cu) and 0.12 wt % Cu in the oil.

The S_{Ln} value is only slightly dependent on H_2 pressure. The level of selectivity, however, is lower than that reported for soybean oil hydrogenation. The difference is to be ascribed to the different oil compositions and not to the catalyst used. Values from different oils cannot be compared. The product composition at different stages of the reaction at 6 atm is shown in Figure 5. The initial increase of the percentage of linoleic acid ester (ca. 1–2%) is fully comparable with that of a typical soybean oil hydrogenation.

Basic Principles for the Catalyst Preparation

The catalyst preparations described here are based on the following assumptions. The first copper ions that are adsorbed onto the silica gel from the ammoniacal solution are bonded directly to the support material and will constitute the oxidic part of the partly reduced catalyst surface. The strength of the bonds between the copper ions and the support depends on the excess of NH_4OH in the adsorption solution. A low excess results in relatively weak bonds, like those of impregnation. The copper precipitated onto the gel by dilution of the ammoniacal solution forms less stable CuO crystals at the surface. Thus, a catalyst surface produced from a solution with a low concentration of copper and a high excess of NH_4OH shows predominantly oxidic properties.

Conditions of Cu Adsorption

The composition of the adsorption solution (the Cu/NH_4OH ratio and the amount of copper charged) was varied in a series of catalyst preparations. The activity values of the catalysts produced were evaluated in rapeseed oil hydrogenation; 8 g of catalyst material was charged per 300 g of oil. The catalyst activity per wt % Cu in the oil as a function of excess NH_4OH in the adsorption solution is shown in Figure 6. The activity is estimated as $100/(t_{15} \cdot C_{Cu})$, min $^{-1}$, where t_{15} is the time required for an iodine value drop of 15 units, min, and C_{Cu} is the amount of Cu charged in the oil, wt % Cu. The excess of NH_4OH has been calculated on the basis that every Cu^{II} ion corresponds to four NH_3 molecules.

The catalyst activity per unit Cu increased with the excess of NH_4OH. If too strong an alkaline solution was used, it resulted, however, in an almost inactive catalyst. The maximum percentage of conjugated dienes formed during hydrogenation increased with the excess of NH_4OH, which is in accordance with the assumption that the surface is getting more and more oxidic properties.

The most active catalyst was prepared in the following manner: 5.75 ml of an ammonium hydroxide solution (25 wt % NH_4OH) was added to 100 ml of water containing 2 g of $Cu(NO_3)_2 \cdot 3H_2O$. Ten grams of silica gel was added and the volume was diluted to 800 ml with water. The colorless liquid was poured off and a new batch of the cooper solution was added to the gel. The volume was increased to 1600 ml before filtration, washing with water, drying at 110 C over night, and calcination in air at 350 C for 2 hr. The catalyst contained ca. 10 wt % Cu.

In the actual rapeseed oil the maximum activity, which was obtained with a NH_4OH excess of 4.0 mole/liter, was about two times the activity of the catalyst prepared with a

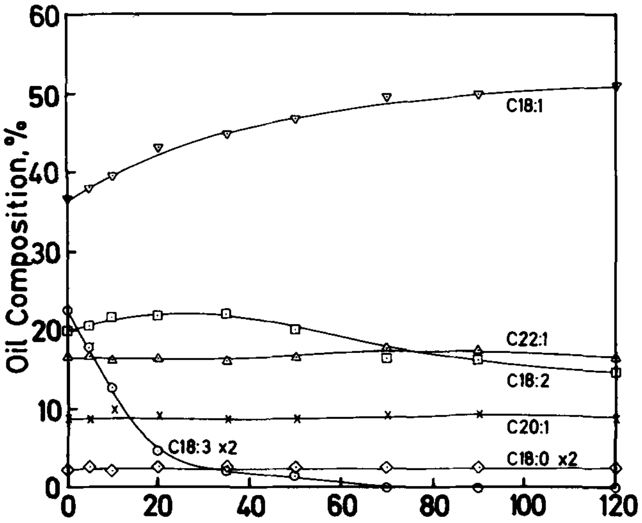


FIG. 5. The GLC-composition of rapeseed oil during hydrogenation with Cu/SiO_2 (17% Cu) at 6 atm and 185 C; 0.12 wt % Cu in the oil.

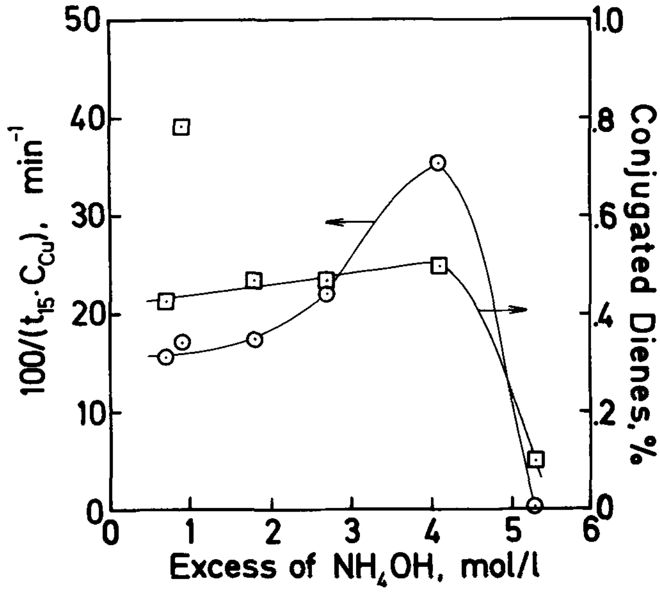


FIG. 6. Catalyst activity per wt % Cu in the oil and conjugated diene formation as a function of excess NH_4OH in the adsorption solution; rapeseed oil hydrogenation at 6 atm and 185 C.

NH_4OH excess of ca. 1.8 mole/liter solution, which was used in the procedure given by Koritala.

Mixtures of Two Catalysts

In the proposed reaction model, the catalyst surface represents two properties. The fatty molecules need not desorb between the conjugation and the hydrogen addition steps. However, one possibility for improving the activity per g of copper charged into the oil consists of combining two catalyst materials; one is constructed to produce conjugated dienes (the oxidic component of the surface) and the other one to hydrogenate the conjugated dienes produced (the copper metal component). In such a system, the fatty molecules have to desorb and re-adsorb before the reaction is completed. The advantage of such a catalyst system is that the two catalyst phases may be optimized independently.

Experiments were carried out with a mixture of two Cu/SiO_2 catalysts. Type I, in which the copper is more strongly bonded to the support, was represented by the catalyst supplied from Grace & Co. (4% Cu). Type II, which also contains copper with weaker bonds to the support, was represented by the Cu/SiO_2 catalyst containing 17% Cu. The time required for an iodine value drop of 15 units in rapeseed oil with a catalyst mixture, where the ratio between the amounts of copper charged as I and II was 2:1, was 47% shorter than if the same amount of copper was charged as catalyst I only and 34% shorter than if all the copper was charged as catalyst II (Fig. 7).

Metal-promoted Cu/SiO_2 Catalyst

The catalyst activity is highest during catalyst reduction. Accumulation of conjugated dienes indicates however a hydrogen shortage on the catalyst surface. The supply of dissociatively adsorbed hydrogen can be increased by addition of a metal that has an unfilled d-orbital.

The method of catalyst preparation involving NH_4OH allows the addition of metals other than copper, provided that the metal hydroxides are soluble in an NH_4OH excess. Studied here were the effects of the additions of chromium, cobalt and zinc from the first long period and silver from the second one. Two wt % metal based on the amount of copper was added to the adsorption solutions resulting in a catalyst with 17 wt % Cu. From the results of Moulton et al. (15) concerning the addition of nickel to a CuCr-catalyst, the effect of a nickel addition was regarded as known. Due to the risk of contaminating the autoclave with this active but hardly selective metal, nickel was avoided in the experiments.

The promoted catalysts were tested in soybean oil hydrogenation. Only the addition of cobalt gave an enhanced catalyst activity (Fig. 8). The selectivity S_{Ln} was as high as that of the original Cu/SiO_2 catalyst in soybean oil ($S_{Ln} = 10.9$). From a technical point of view, the increase of activity by the addition of cobalt was regarded as too small to be of practical interest. The toxicity of cobalt is unfavorable as well.

Comparative Tests

The copper chromite catalyst, Harshaw Cu-1106P, used for comparison in this report was the best catalyst in a comparison test performed at this laboratory using soybean and rapeseed oil hydrogenation. Ten commercially supplied catalysts, selected from different catalyst firms, were tested. The comparison took into consideration the activity per wt % Cu in the oil, noted as the ratio $100/(t_{15} \cdot C_{Cu})$, min^{-1}. The reaction conditions were 6 atm H_2 pressure, 185 C, and a hydrogen flow of 50 liter/hr. The re-use properties were not considered.

The comparative tests presented here included four different catalysts. (A) Cu-1106P – 29.9% Cu; (B) Cu/SiO_2 (Koritala) – 16.8% Cu; (C) Cu/SiO_2 – 10.1% Cu; (D) Cu/SiO_2 (mixture) – 6.7% Cu. The preparation of the catalyst C was described earlier in this report as well as the composition of the catalyst mixture D.

Table I shows the result of a comparison between the catalyst A and B. These catalysts are rather equivalent in the respect of soybean oil, but the Cu/SiO_2 catalyst offers considerable advantages in the hydrogenation of rapeseed oil.

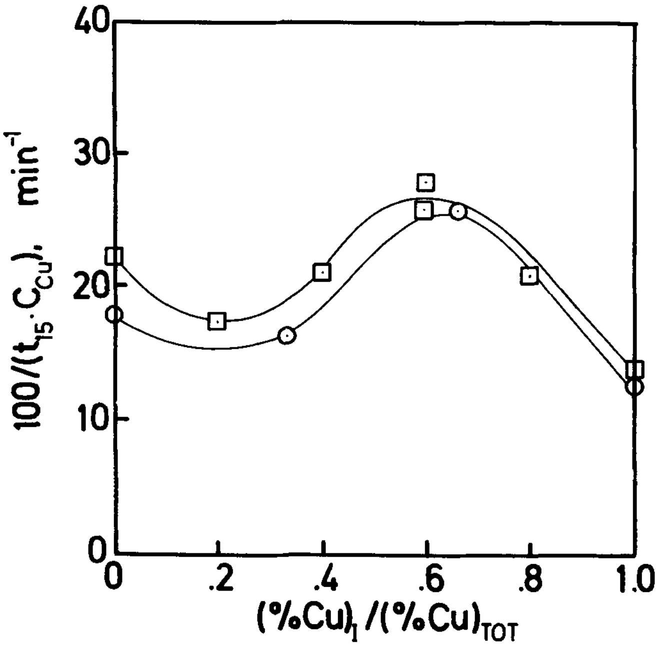


FIG. 7. Catalyst activity vs. the fraction of copper charged as catalyst Type I, containing 4% Cu (0.15 wt % Cu in rapeseed oil, 6 atm, and 185 C; two series of experiments, one of which with more experimental points).

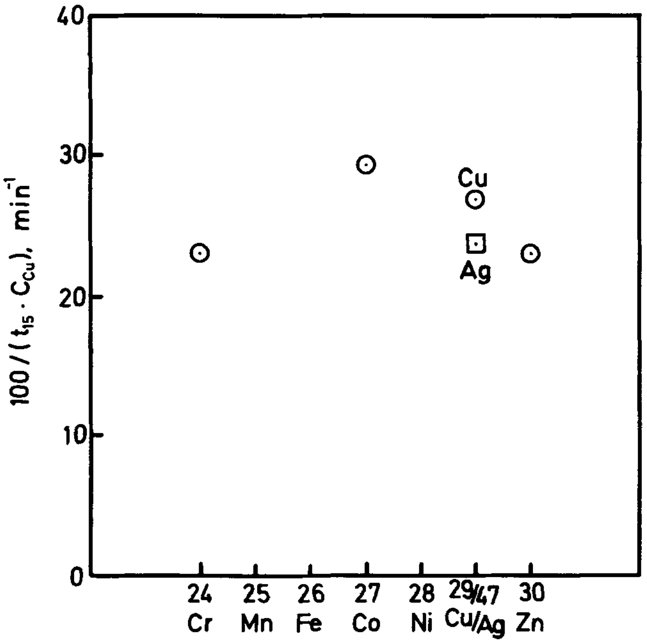


FIG. 8. Promoted Cu/SiO_2 catalyst (0.13 wt % Cu in soybean oil, 6 atm, and 185 C).

TABLE I

A Comparison between the Cu-1106P and Cu/SiO_2 Catalysts in the Hydrogenation of Soybean and Rapeseed Oils (6 atm and 185 C).

Oil	Catalyst[a]	C_{Cu}[b] %	t_{15} min	$\frac{100}{t_{15} \cdot C_{Cu}}$ min^{-1}	S S_{Ln}
Soybean	A	0.20	21	24	9.7
Oil	B	0.15	30	22	9.8
Rapeseed	A	0.20	83	6	6.8
Oil	B	0.15	34	20	7.5

[a] A = Cu-1106P; B = Cu/SiO_2 – 16.8% Cu.

[b] C_{Cu} = wt % Cu in the oil.

The four catalysts A-D were compared in rapeseed oil hydrogenation (Table II). In comparison with the oil of Table I, the oil used here contained less catalyst poison (Cu-1106P, 0.20 wt Cu, 185 C and 6 atm: $100/(t_{15} \cdot C_{Cu})$ = 6 min^{-1} and 10 min^{-1}, respectively). The copper content is best used in the form of Cu/SiO_2 (10.1% Cu). However, the catalyst B and D were rather equivalent in this test. The result is opposite to the results of the experiments in Figure 8, where the catalyst mixture D was superior to B. Thus, the order of precedence of the catalysts is not absolute, but may vary depending on the type and concentration of dominating catalyst poisons in the rapeseed oils.

The difference between copper chromite and Cu/SiO_2 catalysts in rapeseed oil hydrogenation is partly ascribed to the resistibility of catalyst poisoning. The reaction time t_{15} in the hydrogenation of rapeseed oil with Cu-1106P was reduced to one third if the oil was subjected to degassing at 185 C prior to the charging of catalyst (13). The corresponding reduction of the reaction time t_{15} with Cu/SiO_2 (B) in the same rapeseed oil was only ca. 20% (33 to 27 min). The poisoning effect of volatile oxidation products is thus considerably lower with the use of Cu/SiO_2 catalysts.

Concerning the selectivity S_{Ln}, there is no difference between the four tested catalysts.

Product Evaluation

A sample of the rapeseed oil type Lowbra was hydrogenated in the test-autoclave (4 x 300 g) with the catalyst mixture D. The product obtained was evaluated for fatty acid composition and organoleptic quality. The process conditions were: 0.1 wt % Cu in the oil, 185 C, 6 atm, 1700 rpm, and 50 liter H_2/hr. The reaction was interrupted after 35 min. The oil was cooled and filtered through Celite. Citric acid was added in an amount corresponding to 120 ppm. The hydrogenated oil was bleached and deodorized together with a reference sample, consisting of original bleached rapeseed oil.

TABLE II

A Comparative Catalyst Test in Rapeseed Oil at 6 atm and 185 C.

Catalyst[a]	Amount of catalyst g/300 g	C_{Cu}[b] %	t_{15} min	$\frac{100}{t_{15} \cdot C_{Cu}}$ min^{-1}	S_{Ln}
A	1.2	0.12	120	7	5.0
B	1.8	0.10	55	18	5.3
C	3.0	0.10	40	25	5.3
D	4.4	0.10	62	16	5.3

[a] A = Cu-1106P, B = Cu/SiO_2 –16.8 % Cu, C = Cu/SiO_2 – 10.1 % Cu and D = Cu/SiO_2 (mixture) –6.7% Cu.

[b] C_{Cu} = wt % Cu in the oil.

The hydrogenation process included an iodine value decrease from 108.7 to 95.8 (method according to Hanus). The change of fatty acid composition is shown in Table III, which also includes the anisidine values (AV), the peroxide values (PV), free fatty acid values (FFA), and the color values (Lovibond 5¼") of the reference substance and the Cu-hydrogenated oil, both after bleaching and deodorization. The selectivity S_{Ln} towards the linolenate was 7.1. The copper content of the oil at different stages during processing changed according to Table IV (atomic absorption spectroscopy).

The Cu-hydrogenated rapeseed oil was compared to the reference substance by a taste panel in a short-time test. According to the procedure used, the oil samples were kept in open pots at 50 C between the flavor evaluations (Table V).

No hydrogenation taste was noted. The hydrogenation step increased the oil stability towards oxidation even if the difference between the hydrogenated and unhydrogenated oil was smaller than expected. However, the result is consistent with new findings that a good quality raw

TABLE III

Fatty Acid Composition and Other Data of Unhydrogenated and Cu-Hydrogenated Rapeseed Oils in the Product Evaluation Test

Oil	Reference oil, bleached	Cu-hydr. oil, bleached	Reference oil, deod.	Cu-hydr. oil, deod.
IV (Hanus)	108.7	95.8		
GLC				
C16:0			4.1	4.2
C18:0			1.8	1.7
C18:1			60.3	69.4
C18:2			19.7	19.3
C18:3			8.2	0.5
C20:0			1.1	0.7
C20:1			3.1	2.4
C22:1			0.5	0.3
AV	2.0	0.4	1.3	0.4
PV	0.0	0.0	0.0	0.0
FFA	0.07	0.12		
Color	7.0 x 1.2 = 19.0	1.8 x 0.7 = 8.8	2.0 x 0.6 = 8.0	2.0 x 0.6 = 8.0

TABLE IV

Copper Content of the Rapeseed Oil Used in Product Evaluation

Oil	Cu content, ppm
Raw oil	0.04
Oil before hydrogenation	0.005
Cu-hydrogenated oil after filtering	0.20
Cu-hydrogenated oil after bleaching	<0.004
Reference oil after bleaching	<0.004

TABLE V

Flavor Stability of Cu-Hydrogenated Rapeseed Oil

	Flavor scores[a]	
Days, 50 C	Ref. oil, deod.	Cu-hydr. oil deod.
0	4.7	5.3
1	4.0	3.8
3	3.0	3.6

[a] Scores 1-7, 7 = oil free from flavor and odor

oil, which is carefully refined and deodorized, often shows good stability towards oxidation even without a hydrogenation step. The removal of copper catalyst from the oil causes no problem. Bleaching with a citric acid addition reduces the copper content below the level of detection, 0.004 ppm.

DISCUSSION

The similarities between the behavior of the copper chromite catalyst and the Cu/SiO_2 catalyst containing ca. 17% Cu are obvious. This condition could mainly be ascribed to the fact that the copper of the two catalysts is charged into the oil in its divalent state and that the reduction of the copper during hydrogenation proceeds through the same degrees of oxidation. The reduction potential is influenced by the hydrogen concentration in the oil, which is nearly proportional to hydrogen pressure in the gaseous phase. Independent of the catalyst charged, water is generated during the catalyst reduction, and the effect of catalyst poisoning is to be found as long as this reduction water remains within the oil phase.

The conclusions previously drawn concerning the active phase of copper in the hydrogenation of vegetable oils, based on the experimental work with the copper chromite catalyst (3,4), may be supplemented and summarized in the following manner. The Cu^{II} ions of the copper chromite and the Cu/SiO_2 surfaces are not resistant to reduction, thus the active phases must consist of Cu^{I} compounds and/or Cu^{o}. Judging from the changes of the catalyst activity during the hydrogenation at low pressure levels, activity is first obtained from the catalyst subjected to reduction and then eventually from the metal-reduced form of catalyst, i.e., Cu/Cr_2O_3 and Cu/SiO_2 of which a minor part of the copper still is bonded chemically to the oxidic supports. The rate of reaction over a surface consisting of only Cu^{o} atoms, which thus represents the totally reduced surface without any support, is low at low pressure levels (3). The Cu/SiO_2 and the copper chromite catalysts are rather equivalent in soybean oil hydrogenation, while the former type of catalyst is superior in rapeseed oil hydrogenation. To what extent the difference in rapeseed oil is dependent on the fact that the copper content of Cu/SiO_2 is more resistant to reduction, according to the X-ray diffraction analyses, is not fully clear. However, part of the difference found depends on the varying resistability to catalyst poisoning.

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REFERENCES

1. De Jonge, A., J.W.E. Coenen, and C. Okkerse, Nature 206:573 (1965).
2. Koritala, S., and H.J. Dutton, JAOCS 43:86 (1966).
3. Johansson, L.E., and S.T. Lundir, JAOCS 56:974 (1979).
4. Johansson, L.E., JAOCS 56:987 (1979).
5. Smith, G.W., and L.H. Reyersson, J. Am. Chem. Soc. 52:2584 (1930).
6. Kolthoff, I.M., and V.A. Stenger, J. Phys. Chem. 36:2113 (1932).
7. Kolthoff, I.M., and V.A. Stenger, Ibid. 38:475 (1934).
8. Anderson, Jr., J.H., J. Catal. 23:76 (1973).
9. Burwell, Jr., R.L., Chem. Tech. 1974:370 (1974).
10. Voge, H.H., and L.T. Adkins, J. Catal. 1:171 (1962).
11. Koritala, S., JAOCS 47:106 (1970).
12. Koritala, S., Ibid. 49:83 (1972).
13. Johansson, L.E., and S.T. Lundin, JAOCS 56:981 (1979).
14. Butterfield, R.O., and H.J. Dutton, JAOCS 44:549 (1967).
15. Moulton, K.J., R.E. Beal, and E.L. Griffin, Ibid. 50:450 (1973).

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