Copper Catalysts in the Selective Hydrogenation of Soybean and Rapeseed Oils: I. The Activity of the Copper Chromite Catalyst

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ABSTRACT

In the hydrogenation of soybean and rapeseed oils with fresh copper chromite catalyst, the rate of reaction -d(IV)/dt varies extensively with time. These variations are ascribable to changes in phase composition of the catalyst during its reduction. This reduction is not restricted to an initial period but proceeds in two steps during the major part of a normal hydrogenation for the reduction of the linolenate content of the oil. Variations of the catalyst activity followed by experimental measurements have been related to the changes of the catalyst composition.

INTRODUCTION

The most selective catalysts for the reduction of the linolenic compound in fatty oils such as soybean and rapeseed oils are copper catalysts. Monoenes are not reduced which is why hydrogenation may be performed without increasing the amount of saturates in the oil (1,2). Different copper catalysts have been tested and the selectivity characteristics are practically independent of the type of catalyst. These properties may therefore be ascribed to the copper part (2). Whether it is the elementary form of copper or an oxidized form that contributes most to the activity of the catalyst in selective hydrogenation is, however, still under discussion.

Adkins et al. (3,4) found in 1931 that the copper in the copper chromite catalyst, prepared according to Lazier, was reduced from the divalent state to the monovalent or the elementary state during its use as a hydrogenation catalyst. The reddish compound formed was inactive in hydrogenation reactions (5). They presented a modified copper chromite catalyst containing barium chromate as a stabilizing agent (4). The active form of copper, according to Adkins et al., should thus be copper(II). Koritala and Dutton hydrogenated soybean oil with sodium borohydride-reduced catalysts (1). A black precipitate, presumably copper(II)oxide, turned red after partial reduction of the oil and then became inactive. Addition of chromium stabilized the catalyst. Okkerse et al. (2) used a Cu-Mg-SiO_2 catalyst for soybean oil hydrogenation. The activity of this catalyst was studied in a vapor phase hydrogenation of cyclohexene in order to avoid the diffusion limitation of a liquid phase hydrogenation. The activity was found to increase as the mean state of oxidation of the copper catalyst decreased. This indicates that the active center consist of copper metal crystallites.

Derouane et al. (6) studied a similar catalyst (Cu-MgO) in the hydrogenation of ethylene. The copper oxides, the metallic copper, or the magnesium oxide itself showed no or minimal activity in comparison to the active catalyst. On the basis of the ESR and kinetic data, surface Cu^{2+} ions were proposed as the active species.

The opposing views in literature on the active species of copper catalysts may partly depend on the fact that these catalysts are used for hydrogenation under quite varied conditions. The copper chromite catalyst was originally tested by Adkins at hydrogen pressures above 100 atm. Much work has been done at these high pressure levels. The general opinion seems to be in accordance with the theory of Rabes and Schenck (7) that the active substance in copper chromite catalysts at high pressure levels is the metallic copper formed during hydrogenation. The selective hydrogenation of vegetable oils is normally performed at hydrogen pressures lower than 10 atm under conditions in which the rate of catalyst reduction is low and, consequently, an oxidized state of copper may contribute to the activity of the catalyst. The reaction rate during a fat hydrogenation process with a fresh copper catalyst varies considerably. To a certain extent, this effect is due to the change of the fatty acid composition of the oil. Vigneron et al. (8) have noted that the activity of the copper chromite catalyst was high during linolenate reduction but diminished quickly after the linolenate content dropped to ca. 1%. On the other hand, Koritala et al. (9) have reported that if linolenate and linoleate isomers are reduced separately, the hydrogenation rates are nearly equal.

Before use, the copper chromite catalyst consists essentially of two phases, copper(II)oxide and copper(II)chromite (10). The reduction during its use as a hydrogenation catalyst depends on the conditions, but when completely reduced, it consists of metallic copper on Cr_2O_3 (7, 11). This part of our study on the selective hydrogenation of soybean and rapeseed oils concerns the relationship between the reduction of the copper chromite catalyst and the catalytic activity.

EXPERIMENTAL PROCEDURES

Material

Hydrogenation was carried out with commercially refined and bleached soybean and rapeseed oils. The erucic acid content of the latter oils was ca. 17%.

Two commercially supplied copper chromite catalysts from Harshaw Chemical Company have been used. Normally, Cu-1106 P (40% CuO, 47% Cr_2O_3 and 10% BaO) was used due to its high activity. But for ESCA and electron microscopy experiments, Cu-1800P (51% CuO and 47% Cr_2O_3) containing only two crystalline phases was used.

Analytical Methods

Methyl esters were prepared from oil samples with dimethyl carbonate and sodium methylate catalyst. The methyl esters were analyzed with a 9 ft x 1/8 in. stainless steel column packed with 7% BDS on 80/100 Chrom W and a flame ionization detector.

Iodine values were determined according to the Wijs method (12). The percentage of conjugated dienes was calculated from the UV absorption at 232 nm (12). When specified in the diagram, the effect of conjugated dienes on the volumetric iodine value has been estimated as 0.86 x (% conjugated dienes) on the basis that a system of two conjugated double bonds adds only one halogen molecule. The effect of the conjugated dienes on the calculated iodine value has been estimated with the assumption that all conjugated diene molecules have the same retention time as nonconjugated trienes. The error introduced by this simplification is negligible in this connection (less than 1.0 unit at 3 atm H_2 pressure).

The X-ray diffraction analyses were performed with a Philips PW 1050/25 diffractometer (Cu-K radiation, 45 kV and 24 mA). Using barium chromate phase as the internal standard, the amount of crystalline copper metal in the samples of used Cu-1106P catalyst had been estimated in the following manner. The diffraction angle interval 40.8 - 45.0 °2θ was scanned by steps of 0.05 °2θ. The number of pulses during 1 min was registered. The interval 42.5 - 45.0 °2θ (A) represents the highest interference of copper metal (111) and copper(II)chromite (400). The interval 40.8 - 42.4 °2θ (B) represents the highest interferences of barium chromate (Fig. 1). The amount of copper metal was estimated from the numbers of pulses N_A and N_B' with corrections for background intensities. Calibration was performed using mixtures of copper metal (electrolytic) and an unused catalyst as standard substances.

ESCA measurements were performed with AEI ES 100 electron spectrometer equipped with a hemispherical electrostatic analyzer. Oil pumps fitted with cold traps produced a vacuum of 10^{-7} Torr during the measurements. All spectra were obtained with Al K-radiation (1586.6 eV). The catalyst samples were placed on a platinum gauze during the measurements. The spectra obtained were interpreted with the help of the spectra given by Schön (13).

To make ESCA measurements possible, samples of used catalyst were washed free from fat in chloroform for 72 hr in a Soxhlet apparatus. To prevent oxidation as much as possible, the catalyst samples were kept in chloroform and applied to the platinum gauze as a chloroform slurry just before placing it into the apparatus.

Equipment and Operating Procedures

Hydrogenations were carried out in a 1 liter Parr apparatus 4521. The oil to be hydrogenated and the appropriate amount of catalyst were charged into the autoclave. The oil and catalyst mixture was flushed with nitrogen by bubbling the gas through the oil. During the heating-up period, the oil was stirred at reduced pressure (ca. 6 Torr). The reaction was started by admitting hydrogen gas into the autoclave.

Oil samples were taken under a blanket of nitrogen gas and were immediately cooled to 0 C to prevent oxidation. The catalyst and the oil were separated in a centrifuge at 5000 rpm in nitrogen.

In all the experiments described 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).

According to the mass transfer conditions in this study, the volumetric mass transfer coefficient was found to be ka = 0.65 sec^{-1}. This has been determined with the use of a nickel catalyst according to a method described by Pihl and Schöön (14). By using that value of ka, the concentration difference of hydrogen across the transport film near the gas bubbles could be estimated. In a majority of the experiments, the rate was so low that there was no need to correct for the influence of the external mass transfer resistance. The highest rate obtained corresponded to a concentration difference of ca. 6% of the hydrogen solubility at the actual pressure level.

RESULTS

The Reaction Rate Regions of the Hydrogenation Process

The rate of reaction -d(IV)/dt of a hydrogenation process with fresh copper chromite catalyst decreases after ca. 20 min. This is demonstrated by a number of graphs of soybean oil hydrogenation with varying amounts of Cu-1106P catalyst (Fig. 2). No correlation has been found between the position of the transition point B and the composition of the oil. The iodine value drop of part AB in the process is, however, almost proportional to the amount of catalyst (Fig. 3), which indicates a correlation between the typical shape of the iodine value graphs and the solid phase.

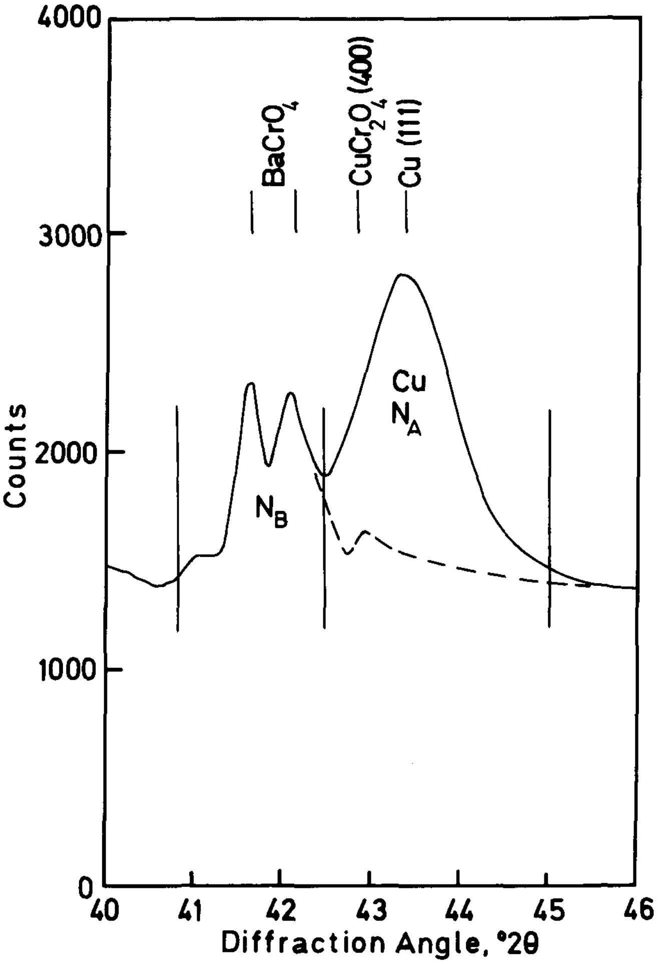

FIG. 1. X-ray diffraction spectrum of used Cu-1106P catalyst showing the method of quantitative copper metal determination. The dotted line represents the spectrum of the fresh catalyst.

For a rough estimation of the changes in the rate of reaction, the iodine value graphs may be divided into three periods. The reaction rate -d(IV)/dt of the three parts AB, BC, and CD varies at three levels in the approximative ratios 6:2:1. The first part AB includes a minor induction period even with increased amounts of catalyst.

The iodine value graph of a hydrogenation with the Cu-1106P catalyst (0.1 wt-% Cu in the oil) at 185 C and 3 atm H_2 pressure, which were the conditions used in several experiments in this report, was determined by frequent samplings of oil. The iodine values of these samples were determined both according to the Wijs method and calculated from the GLC composition (Fig. 4). The shape of the iodine value curve was found to be independent of the method used. The curve reaction rate vs. time was obtained from the slope of the iodine value graph (Wijs). Two distinct periods of relatively high rate appeared (Fig. 5). The reaction rate increased after ca. 60 min, which indicated a third period.

Changes in Catalyst Activity during the Hydrogenation

Since the mass transfer resistance may be neglected in these experiments, the reaction rate -d(IV)/dt at constant temperature and hydrogen pressure is a function of the catalyst activity and the fatty acid composition of the oil. The activity of the catalyst at different stages of reduction has been determined directly at constant fatty acid composition according to the following procedure. A number of hydrogenation runs with fresh catalyst is interrupted at different reaction times. The catalyst of each run is separated from the oil in a centrifuge at 6000 rpm and charged into a portion of the original oil. This second hydrogenation run for activity measurement purposes is performed at fixed standard conditions of 185 C and 6 atm. The activity of each catalyst sample is estimated as $1/t_y$ min^{-1}, where t_y is the time required for an iodine value drop of y units in the second hydrogenation run. The influence of the oil composition and the reduction water is thus eliminated. The activity of the used catalyst samples is given in relation to the activity of the unused catalyst under the conditions of the second run.

Different values of the quantity y have been tested. A too low value of y presents a too small iodine value drop. A too high value presents a risk of missing a sharp activity period. A value y = 3.0 units has been chosen for the activity measurements. The reaction time t = 0 means that the hydrogenation process was interrupted just before the moment when hydrogen gas normally is introduced into the converter. Aside from a minor loss of catalyst material during the experimental work, the activity reduction of the heating-up period includes the effect of initial catalyst poisoning.

The activity of the Cu-1106P decreased to ca. 50% during the heating-up period prior to a hydrogenation run of soybean oil (Fig. 6). The three periods of activity which occur correspond to the three regions of reaction rates appearing in Figure 5. The third activity period represents the final state of the catalyst.

The corresponding curve of the same catalyst used in rapeseed oil at 6 atm H_2 pressure, which was determined for the time interval 0-60 min, is similar to that of soybean oil in the respect of the second activity maximum. The first maximum is considerably lower at y = 3.

The three regions of relatively high reaction rate which were obtained from the slope of the iodine value graph,

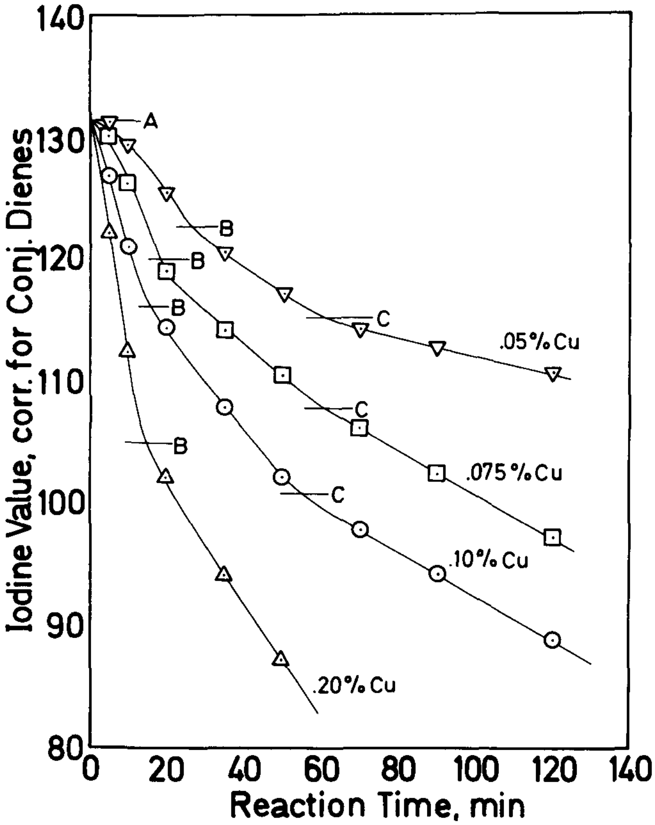

FIG. 2. Effect of catalyst concentration in soybean oil hydrogenation (Cu-1106P catalyst, 6 atm and 185 C; iodine value according to Wijs).

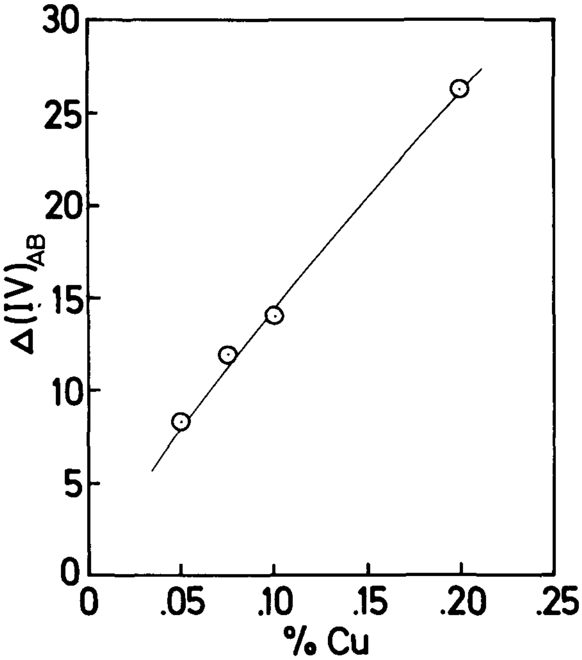

FIG. 3. Hydrogenation of soybean oil with the Cu-1106P catalyst at 6 atm and 185 C; $\Delta(IV)_{AB}$ vs. catalyst concentration.

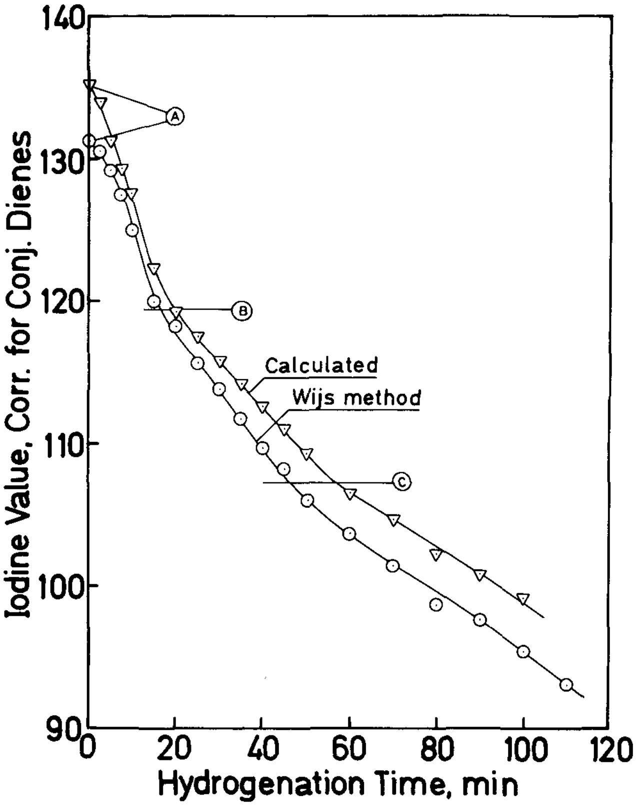

FIG. 4. Iodine value vs. reaction time in the hydrogenation of soybean oil (Cu-1106P, 0.1 wt % Cu in the oil, 3 atm, and 185 C).

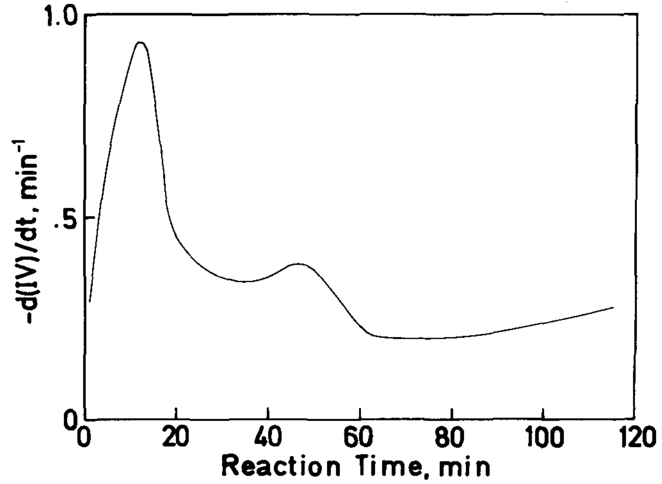

FIG. 5. Hydrogenation rate -d(IV)/dt vs. the reaction time of the hydrogenation run in Fig. 4 (from the IV graph according to the Wijs method).

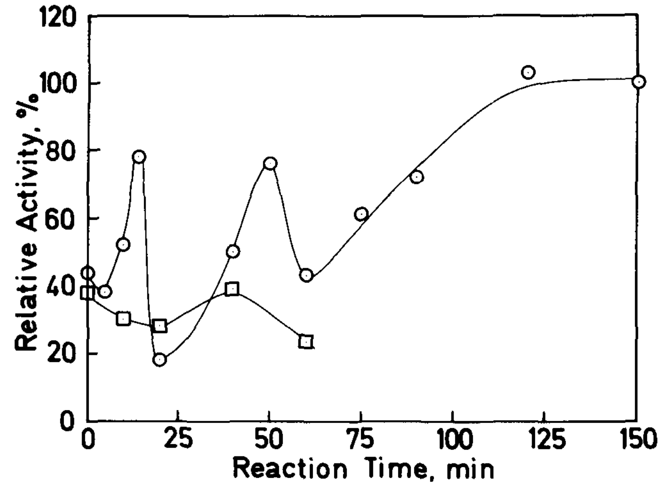

FIG. 6. Relative activity of the Cu-1106P of the Cu-1106P catalyst according to the direct measurement in a second hydrogenation after its use in soybean oil at 3 atm/185 C (○) and in rapeseed oil at 6 atm/185 C (□); 0.10 wt % Cu in the oil. y = 3.0.

thus, correspond to three periods of higher catalytic activity. The explanation for the variation in catalyst activity is found in the changes of the catalyst composition during the hydrogenation process.

The Phase of the Copper Chromite Catalyst

The copper chromite catalyst is usually produced from the precipitate $Cu(OH)NH_4CrO_4$ by decomposition in air at 350-500 C for ca. 2 hr. It is clear from the X-ray diffraction analysis that two separate crystalline phases (CuO and $CuCr_2O_4$) are formed (10).

The Cu/Cr ratio of the Cu-1800 catalyst is consistent with that of a catalyst prepared from the precipitate $Cu(OH)NH_4CrO_4$. Approximately 63 wt % of the material constitutes the $CuCr_2O_4$ phase, which is insoluble in hot 6 N HCl. From the amounts of copper and chromium leached in the acid solution it follows that ca. 15 wt % of the chromium does not form the $CuCr_2O_4$ compound. The intimate contact between the CuO and the $CuCr_2O_4$ phase is clear from the fact that the catalyst material, when heated to 960 C for 5 hr, reacts to form $Cu_2Cr_2O_4$ in a solid phase reaction. After such a treatment, only ca. 5% of the copper present is still soluble in hot 6 N HCl.

Three different types of particles appear in the electron microscopy pictures of the fresh Cu-1800P (Fig. 7). The majority of the material forms aggregates of particles. The second type appears as large, long and thin particles which look like the crystals of the original precipitate. The third type of particles is somewhat smaller and more compact particles existing partly in direct contact with the aggregates. The second and third type of particles dissolve in 6 N HCl. The first type of particle aggregates is only partly dissolved. A careful study of the changes which occur within the granular structure during HCl-leaching reveals small HCl-soluble crystallites which thus constitute the CuO phase.

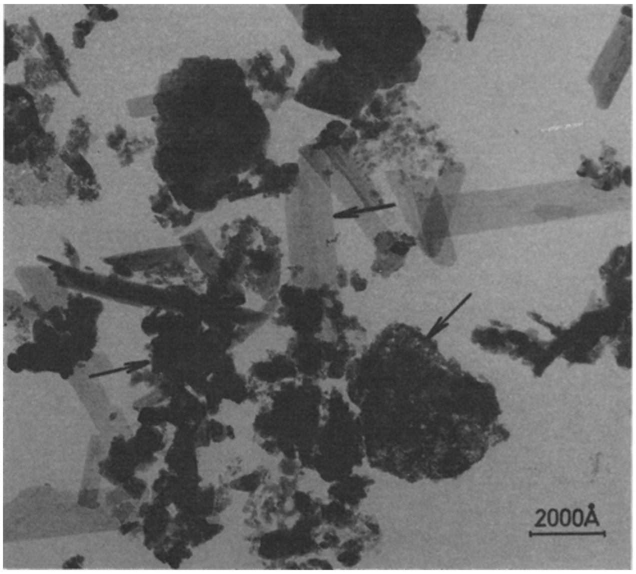

FIG. 7. Cu-1800P catalyst on carbon film.

The different types of particles represent different stages in the heat activation reaction. The aggregates correspond to formation of copper oxide and copper chromite, while the particles which dissolve in HCl solution represent the least crystalline material. Consequently, two forms of copper metal are formed during the catalyst reduction. The metal formed within the aggregates arises from crystalline phase and are distinguishable from the metal formed from the more amorphous copper chromium oxides of the other types of particles.

Changes in Phase Composition shown by X-ray Diffraction and ESCA measurements

In order to find the correlation between the changes in phase composition and the catalyst activity, X-ray diffraction analysis and ESCA measurements have been used to investigate catalyst samples in the hydrogenation of soybean oil at 3 atm and 185 C. The comparatively low hydrogen pressure was used with the intention of obtaining a slow catalyst reduction.

Samples for the X-ray diffraction analysis represented different reaction times of a hydrogenation with Cu-1106P (0.1 wt % Cu, 185 C and 3 atm). The proportion of copper metal in the catalyst increases rather rapidly during the first 10-15 min (Fig. 8). Simultaneously, the diffraction patterns of copper(II)oxide diminish. No patterns of copper(I)oxide have been observed, and only weak, broad patterns of copper(I)chromite. The curve showing the fraction of copper in metal vs. the reaction time passes a maximum as the hydrogenation process passes the reaction rate maximum just before point B. The highest level is reached at about the same time as the point C is passed. That level, representing ca. 95 wt % of the copper, has been determined from X-ray diffraction analysis of a catalyst sample

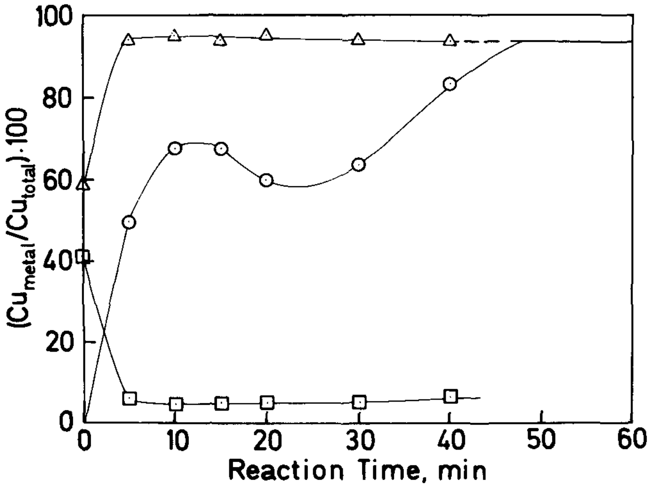

FIG. 8. Changes in the phase composition from the X-ray diffraction analyses (○) and from the solubility data (HCl fraction △ and H_2SO_2 + H_3PO_4 fraction □) Cu-1106P, 0.1 wt % Cu in soybean oil, 3 atm, and 185 C.

reduced during use in soybean oil at 20 atm for 120 min.

The size of the copper crystallites formed varies within the interval 80-100 Å, determined from the peak broadening at 43.3 °2θ.

The ESCA signals arise from a surface layer about 20 Å thick. Provided that the catalyst is free from fat, information is obtained from the part of the catalyst which is in contact with the oil. The samples investigated here represent a hydrogenation during the same conditions as the hydrogenation above. However, the Cu-1800P catalyst was used instead of the Cu-1106P containing also a $BaCrO_4$ phase. ESCA measurements were performed on the $Cu2p_{3/2}$ peak with the adjacent satellite peak (Fig. 9) and the $L_3M_{4,5}M_{4,5}$ Auger electron spectra (Fig. 10).

The satellite peak typical of the Cu^{II} ions is present only in the spectrum of the original catalyst. The peak width of the $Cu2p_{3/2}$ decreases with the reaction time, which indicates the reduction to Cu^0 over Cu^I.

The Auger spectrum of the sample, representing a reaction time of 5 min, indicates the presence of Cu^I. The Auger spectrum of the 50 minutes sample shows the typical resolved fine structure of Cu^0 with a minimal contribution from Cu^I. This contribution may arise from an air-oxidized surface.

Changes in Phase Composition from Solubility Data

Samples of fresh and used Cu-1106P catalyst (0.1 wt % Cu in soybean oil, 3 atm and 185 C) were leached in two manners; in hot 6 N HCl and in a hot 8:3 mixture of concentrated sulphuric acid and 85% ortho-phosphoric acid. The acid mixture dissolves $CuCr_2O_4$ and $Cu_2Cr_2O_4$, but not Cr_2O_3. The amounts of copper dissolved in the two leaching steps were determined by atomic absorption spectroscopy. (The composition of the acid mixture is from reference 15.)

The HCl-soluble copper increases during the first minutes of the hydrogenation from 59% to ca. 95% (Fig. 8). Simultaneously the H_2SO_4+H_3PO_4-soluble fraction decreases from 41% to ca. 5%. Obviously the $CuCr_2O_4$ phase is drastically changed during the initial stage of the catalyst reaction. Copper(I)chromite, produced from $CuO\cdot CuCr_2O_4$ compound by heating at 960 C for 5 hr, dissolves very slowly in 6 N HCl. A monovalent copper chromite phase with a disturbed crystal pattern may behave otherwise. Therefore, the result does not exclude the existence of a reduction intermediate, consisting of $Cu_2Cr_2O_4$ and giving a broad peak in the X-ray diffraction spectra. $Cu_2Cr_2O_4$ dissolves in the acid mixture.

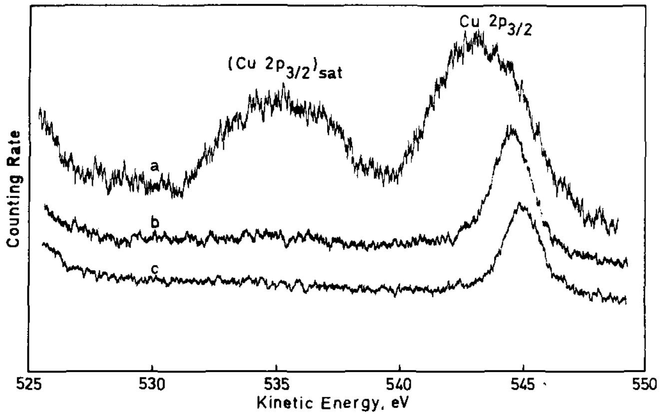

FIG. 9. The $Cu2p_{3/2}$ peak with the adjacent satellite peak of the ESCA spectrum of (a) the original Cu-1800P catalyst, the catalyst used for (b) 5 min and (c) 50 min in a soybean oil hydrogenation at 3 atm and 185 C.

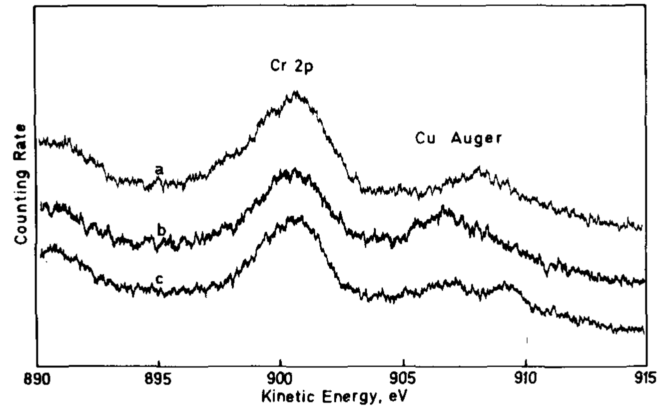

FIG. 10. The Auger electron spectra of the Cu-1800P catalyst: (a) original catalyst, (b) catalyst used for 5 min, and (c) 50 min in a soybean oil hydrogenation at 3 atm and 185 C.

The Behavior of the Different Copper Phase

The copper(II)oxide phase of a lot Cu-1800P catalyst was removed in hot 6 N HCl until the X-ray diffraction spectrum showed no patterns of copper(II)oxide. The $CuCr_2O_4$ powder was tested for catalytic activity for rapeseed oil hydrogenation (6 atm and 185 C). The first activity period of the original catalyst was replaced with an induction period of ca. 20 min (Fig. 11). Maximum activity, corresponding to about one fourth of the activity of the whole catalyst, was obtained after 40 min.

X-ray measurements showed that $CuCr_2O_4$ powder was reduced at a lower rate than the $CuCr_2O_4$ phase of the copper chromite catalyst. The importance of the effect of mixing is further clarified by the fact that the hydrogenation activity of copper oxide is low. For instance, the iodine value decrease of soybean oil in a hydrogenation with 2.5 g of CuO at 6 atm and 185 C for 70 min was only ca. 4 units.

The effect of removing the CuO phase has been studied earlier in other hydrogenation systems, but not in fat hydrogenation (16,17). Questions have been raised as to whether the remaining chloride ions from the HCl leaching might not cause catalyst poisoning. Here the amount of chlorine at the surface of the catalyst grains were unchanged throughout the leaching procedure and the ratio Cu/Cr of the surface was equal to that of the inner part of

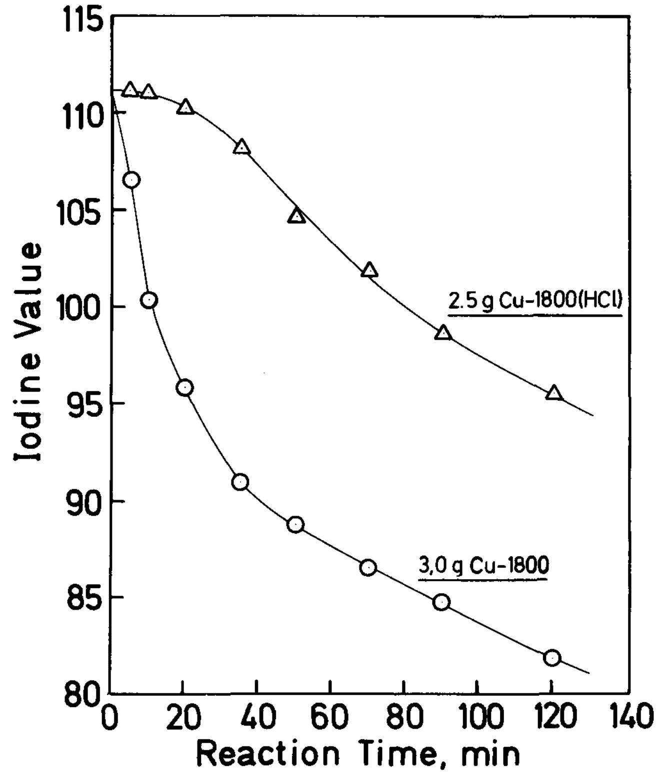

FIG. 11. A comparison between original and HCl-washed Cu-1800P catalyst (rapeseed oil, 6 atm, and 185 C).

the grains (ESCA).

Copper metal, which has been tested for activity in the form of electrolytic Cu and Raney-Cu (18 m^2/g), shows low activity. The selectivity towards the linolenate component of soybean oil is no more than that of nickel catalysts. The substances Cu_2O and $Cu_2Cr_2O_4$ show no or minimal activity. The finely divided copper metal and copper oxide mixture obtained by decomposition of copper(II)oxalate shows no activity at all. Our conclusion is that no one of these separated phases can be the cause of the activity found in the fat hydrogenation with the copper chromite catalyst. The CuO and Cu_2O components are immediately reduced to metal, at least as far as the surface layer is concerned.

Specific Surface Area Measurements

Catalyst samples corresponding to different times of reaction in a hydrogenation of soybean oil with Cu-1800P catalyst (0.2 wt % Cu in the oil, 6 atm and 185 C) were washed in a Soxhlet apparatus until a new portion of chloroform showed no absorption at 220 nm in the UV spectrum. The amount of remaining fat within the catalyst pores was estimated from an analysis of the carbon to be ca. 3.5 wt %, which corresponds to less than 5% of the pore volume. The specific surface areas of the samples were determined according to the BET method (Table I). The reduction of the catalyst occurs without any significant change in the specific surface area.

DISCUSSION

The variations of the catalytic activity during a hydrogenation process with an unused copper chromite catalyst is ascribable to the different stages of the catalyst reduction.

The CuO and the $CuCr_2O_4$ phases exist in contact with each other, which facilitates the reduction of the $CuCr_2O_4$ phase. Stroupe (10) proposed a low temperature version of the reaction between CuO and $CuCr_2O_4$ occurring above 900 C resulting in the formation of $Cu_2Cr_2O_4$:

TABLE I

The BET Surface of Cu-1800P Catalyst Samples from a Soybean Oil Hydrogenation at 6 atm and 185 C

Reaction time min	BET Surface m^2/g
--	32.1
0	32.2
5	31.5
10	31.9
20	31.9
35	30.0
90	30.7

$$CuO + CuCr_2O_4 + H_2 \rightarrow Cu_2Cr_2O_4 + H_2O \qquad 1$$

This reaction can be noted as the sum of the two reactions:

$$CuO + H_2 \rightarrow Cu + H_2O \qquad 2$$

$$Cu + CuCr_2O_4 \rightarrow Cu_2Cr_2O_4 \qquad 3$$

Stoichiometrically, ca. 83% of the existing copper in the Cu-1106P catalyst can react in this way. The excess of CuO is reduced to metal according to the reaction 2 without any interaction with the $CuCr_2O_4$ phase. In a second stage, the $Cu_2Cr_2O_4$ phase formed is reduced to copper metal and chromic oxide:

$$Cu_2Cr_2O_4 + H_2 \rightarrow 2\ Cu + Cr_2O_3 + H_2O \qquad 4$$

The decrease in the amount of copper metal, registered by the X-ray diffraction analyses, could be the result of reaction 3. However, this is inconsistent with the solubility experiments, which seems to show that no $CuCr_2O_4$ phase remains at that stage.

The reduced catalyst, in which ca. 95% of the copper exists as Cu/Cr_2O_3, contributes to the activity to a greater extent first in a stage where water no longer is being generated. This is in agreement with the fact that water is known first of all as a poison to the reduced copper catalyst. The main part of an industrial hydrogenation process with unused catalyst with a reaction time of ca. 60 min is, however, performed with activity belonging to the first two periods.

The Cu^{II} ions on the catalyst surface are reduced already during the first minutes of the hydrogenation process. During the catalyst reduction, the surface layer consists of $Cu_2Cr_2O_4$ and Cu metal. A separate phase of $Cu_2Cr_2O_4$ shows no activity and the activity of Cu metal has been found to be low, especially in the presence of water. Activity is thus to be ascribed to the combination of Cu and $Cu_2Cr_2O_4$. The catalytic activity is strongly related to the reduction of the catalyst. The active species may consist of especially activated copper atoms, e.g., coordinatively unsaturated copper.

The results presented here combine some of the apparently opposing views of literature on the active phase of the copper chromite catalyst by showing that two separate levels of catalyst reduction possess activity.

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