

Copper Catalysts in the Selective Hydrogenation of Soybean and Rapeseed Oils: III. The Effect of Pressure when using Copper Chromite Catalyst

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ABSTRACT

The influence of pressure on hydrogenation is investigated between 2-20 atm. The relationship between rate of reaction and pressure is complex, with a maximum rate at 6 atm in the pressure range below 14 atm. This is because catalyst reduction is simultaneous with fat hydrogenation. Accumulation of conjugated dienes is measured and a suggested mechanism is presented.

INTRODUCTION

Hydrogenation catalysts based on copper possess high selectivity for hydrogenation of the linolenate component of vegetable oils such as soybean, linseed and rapeseed oils. The linolenate is reduced 7 to 12 times faster than linoleate. Monoenes are not reduced, and therefore the percentage of saturates is nearly unchanged during hydrogenation (1,2).

Industrial autoclaves are usually designed for a maximum pressure of 11 atm, and practically applied pressures range from 2 to 7 atm (3). The effect of the hydrogen pressure on the product composition in the hydrogenation of soybean and linseed oils, as well as in the hydrogenation of various pertinent methyl esters, has been studied first of all at these pressure levels. Increasing pressure increases the rate of hydrogenation and decreases the percentage of conjugated dienes in the oil undergoing hydrogenation (4,5). The linolenic acid appears to be reduced primarily through a conjugated intermediate, which is desorbed less readily from the catalyst at a pressure of 5 atm than at 2 atm (5).

The low activity of copper catalysts, which is well known, can be compensated for by an increase in the hydrogen pressure above the interval generally used in the fat industry today. This is shown by the experiments of Mounts et al. (6), which were performed according to the dead-end procedure. The reaction rate is considerably increased by leading a flow of hydrogen gas through the autoclave during the hydrogenation process. Water and oxidation products are continuously removed from the oil and the autoclave, resulting in a decrease of catalyst poisoning (7).

Copper chromite catalysts are reduced during use (8). Catalytic activity coincides partly with the reduction of the catalyst, which proceeds in two periods if the water formed is removed from the oil and catalyst mixture. The reduced catalyst, consisting mostly of $\text{Cu/Cr}_2\text{O}_3$, shows activity first in the stage when the water of reduction has been removed from the oil.

During that part of the process when the catalyst is being reduced, two hydrogen-consuming reactions are occurring at the surface of the catalyst. However, the amount of hydrogen required for the reduction of the catalyst is small in comparison to the amount of hydrogen converted in the hydrogen addition reaction. In a hydrogenation of 300 g oil with 0.1 wt % Cu, charged in its divalent state, the consumption of hydrogen due to the reduction of the catalyst is ca. 0.11 liter of H_2 (STP). An iodine value drop of 15 units corresponds to ca. 8 liters

of H_2 . Thus, less than 2% of the hydrogen consumed is used for the reduction of the catalyst. Such a small proportion may not limit the supply of hydrogen for the hydrogen addition reaction. Concerning the activity of the catalyst, however, the activity contributions associated with the reduction of the catalysts are dominating during the first hydrogenation run of a catalyst lot. The rate of catalyst reduction thus affects the lifetime of the catalyst, and the order of priority between the two hydrogen-consuming reactions is of great importance.

The first step of the hydrogenation process, the reaction of conjugation, does not occur in the absence of hydrogen (9), but it requires no net supply of hydrogen. It is therefore favored on a surface with a low hydrogen coverage. According to the mechanism, often referred to as the Horiuti-Polyanyi mechanism, an adsorbed molecule on such a surface has the choice between taking up a hydrogen atom from the surface or giving a hydrogen atom to the surface (10). If a system of two methylene-interrupted double bonds is adsorbed on a surface with low hydrogen coverage and no hydrogen atoms are available for a complete hydrogenation reaction, a conjugation of the two double bonds is thermodynamically favorable. A high rate of reaction requires a good supply of dissociatively adsorbed hydrogen at the catalyst surface. However, such a good supply also implies the risk of a fast catalyst reduction, which means a lower mean value of catalytic activity. In this report, the conditions of the catalyst surface with respect to the hydrogen coverage are discussed, primarily on the basis of a relation between hydrogen pressure and rate of reaction $-d(\text{IV})/dt$.

EXPERIMENTAL PROCEDURES

Material

Hydrogenations were carried out with commercially refined and bleached soybean and rapeseed oils. The percentage of erucic acid in the different rapeseed oils was ca. 17%.

The catalysts used were two commercially supplied copper chromite catalysts from Harshaw Chemical Company, Cu-1106P (40% CuO , 47% Cr_2O_3 , and 10% BaO) and Cu-1800P (51% CuO and 47% Cr_2O_3), and a Raney-Cu catalyst from the firm Dr. Theodor Schuchardt.

Analytical Methods

Methyl esters were analyzed with a 9 ft. x 1/8 in. column packed with 7% BDS on 80/100 Chrom W. 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 amount of crystalline copper metal in the samples of used Cu-1106P catalyst was estimated from X-ray diffraction measurements with the barium chromate phase as an internal standard (8).

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

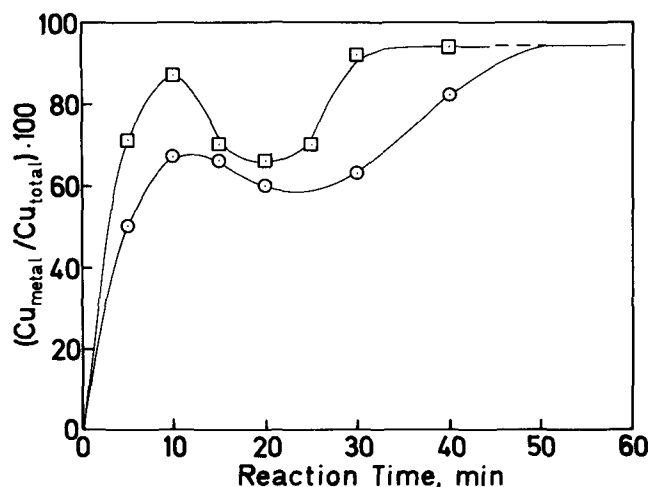


FIG. 1. Copper metal in Cu-1106P catalyst during reduction without hydrogenation (□) and during reduction with a simultaneous hydrogenation reaction (○); 0.1 wt % Cu, 3 atm, and 185 C.

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 of 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 of the gas/liquid interface k_a at the mass transfer conditions in this study has been found to be $k_a = 0.65 \text{ sec}^{-1}$ (7). The experimental results are considered to be independent of the external mass transfer resistances.

RESULTS AND DISCUSSION

The Order of Priority between the Catalyst Reduction and the Hydrogen Addition

The Cu-1106P catalyst, 0.1 wt % Cu in the oil, was reduced at 3 atm and 185 C in a prehydrogenated soybean oil, hydrogenated as far as possible with the same catalyst. The composition of the reduction medium was: C16:0 10.2%, C18:0 3.4%, C18:1 72.5%, and C18:2 12.9%. The iodine value of the oil decreased less than 3 units, and thus the reduction occurred with only a very small simultaneous hydrogen addition reaction. In all other respects the conditions were the same as those of the hydrogenation previously performed for the study of the catalyst reduction during hydrogenation (8). According to the X-ray diffraction measurements, the formation of copper metal proceeds at a higher rate if no fat hydrogenation reaction occurs (Fig. 1). Thus a hydrogen-consuming reaction occurring at the surface decreases the potential of catalyst reduction. The final reduction level is the same irrespective of whether hydrogenation occurs at the surface or not. The bleached soybean oil used in these experiments was very easily hydrogenated, and therefore the effect of catalyst poisoning on the result is regarded as negligible.

The Effect of a Low Hydrogen Coverage

As the mass transfer resistances are negligible, the hydrogen coverage of the catalyst surface depends on the hydrogen concentration in the liquid phase, the ability of the catalyst to adsorb hydrogen from the liquid phase, and the rate of the hydrogen addition reaction.

The influence of a low hydrogen concentration in the

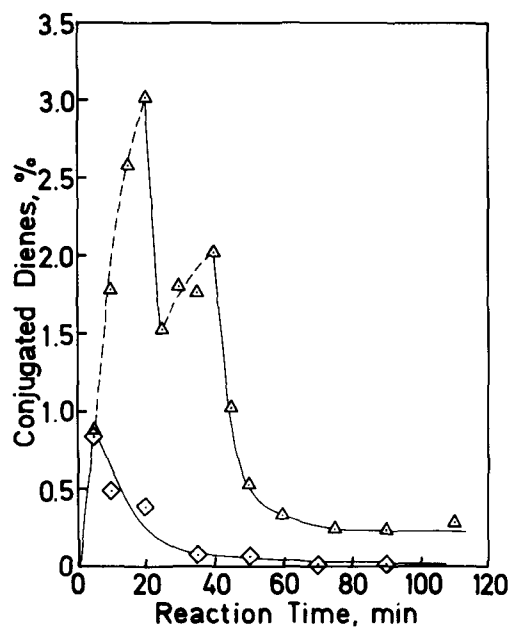


FIG. 2. Accumulation of conjugated dienes during normal operation (—) and during hydrogen shortage (-----) in rapeseed oil (Cu-1106P, 0.2 wt % Cu, 185 C, and max. 6 atm H_2 pressure).

liquid phase was shown experimentally in the following manner: after 5 min of a normal hydrogenation run (rapeseed oil, Cu-1106P, 0.2 wt% Cu in the oil, 185 C, and 6 atm), the hydrogen supply to the autoclave was interrupted for 15 min. The outlet valve remained open until the pressure reached atmospheric level. This procedure was repeated during the next 5-15 min. Samples were drawn every 5 min, when necessary with the help of nitrogen gas.

The amount of conjugated dienes in the oil increased during the periods when the inlet valve was closed and decreased during the normal operation of the autoclave (Fig. 2). Thus, the accumulation of conjugated dienes is not only strongly dependent on the hydrogen concentration of the oil, but also extremely sensitive to variations of that concentration. The formation of conjugated dienes is favored by a low supply of hydrogen at the catalyst surface.

The Formation of Conjugated Dienes

The conjugation reactions start immediately upon the introduction of hydrogen gas to the oil and catalyst mixture. In the hydrogenation with unused copper chromite catalyst, conjugated dienes are formed and accumulated in the oil during the first 10-20 min. The accumulation is different over different systems subjected to reduction. The accumulation of conjugated dienes when a separate copper-(II)chromite phase is used (8) is small compared to the complete chromite catalyst with CuO present. Copper metal (Raney-Cu) forms practically no conjugated dienes at 6 atm (Fig. 3).

The percentage of conjugated dienes in the oil has a maximum, which decreases with the increase of the hydrogen pressure (Fig. 4). The time of the maximum also decreases with increasing pressure. The accumulation is low and independent of pressure at pressures above 13 atm.

The Effect of Pressure on the Rate of Reaction

Soybean oil was hydrogenated with unused Cu-1106P catalyst at different hydrogen pressures (0.05 wt% Cu in the oil). Figure 5 shows the value $15/t_{15} \text{ min}^{-1}$ 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. In flow hydrogenations the hydrogen pressure p_{H_2} is regarded

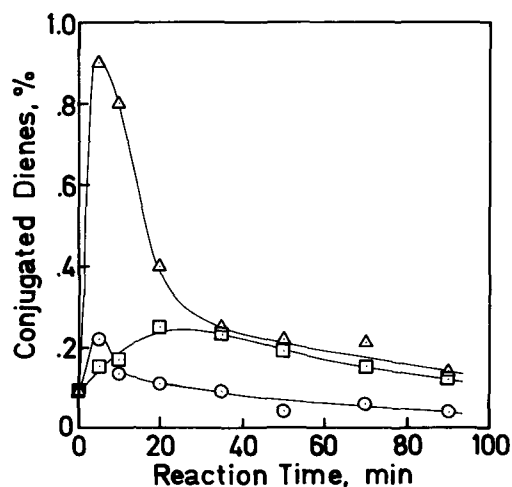


FIG. 3. Conjugated dienes in rapeseed oil during hydrogenation at 185 C and 6 atm with original Cu-1800P, 0.3 wt % Cu (Δ), CuCr_2O_4 , 0.3 wt % Cu (\square), and Raney-Cu 1.2 wt % Cu in the oil (\circ).

equal to the total pressure P . As mentioned in the introductory comments, the curve expresses the influence of two joint effects: the influence of pressure on the reaction rate at constant catalyst activity and the effect of pressure on the average catalytic activity during the first t_{15} min of the hydrogenation at p_{H_2} atm.

The mean rate of reaction increases with pressure up to ca. 6 atm, which is in accordance with the data in the literature. The same normal relation between rate of reaction and pressure is valid above 14 atm. The difference of reaction rate in the different hydrogenation runs remains throughout the whole process, which is shown by the curve $22/t_{22}$ vs. the hydrogen pressure.

The hydrogenation system used includes a hydrogen flow through the oil, which facilitates the removal of reduction water from the oil and the autoclave. The rate of water removal is considerably lower at pressures above the pressure level of saturated water vapor (ca. 11 atm/185 C and ca. 15 atm/200 C). The poisoning effect of water cannot be avoided to the same extent at hydrogenation above that level as is the case at lower pressures. The marked change of the graphs at 11-12 atm/185 C and 15-16/200 C, respectively, is the result of the water effect.

Catalytic activity is ascribed to the surface of an oxidic copper compound subjected to reduction and to the resulting copper metal, promoted by the underlying layer of oxidic support. The rate of catalyst reduction increases with the pressure p_{H_2} . Consequently, the period of activity associated with the catalyst reduction is shorter at high pressure levels. To a certain extent, the effect of a fast catalyst reduction is compensated for by the fact that the rate of hydrogenation with a catalyst with a constant activity increases with pressure. Furthermore, the reduction of the oxidic compound means the formation of copper metal.

Above the pressure level of 12-13 atm the hydrogenation reaction is catalyzed by the reduced form of the catalyst. The mean rate of reaction in the interval 13-20 atm is proportional to $(p_{\text{H}_2}-12)^{0.5}$. The pressure dependence exists mainly during the period of linolenate reduction. A catalyst lot used in a 40 min hydrogenation of soybean oil at 20 atm and 185 C was reused at 10 atm. The low value of $15/t_{15}$ obtained, 0.08 min^{-1} , includes the effect of double catalyst poisoning, but the difference between the oxidic and the reduced catalyst forms is fully clear. The metallic component contributes to the activity at pressures above 10-11 atm, but its contribution is decisive first at ca.

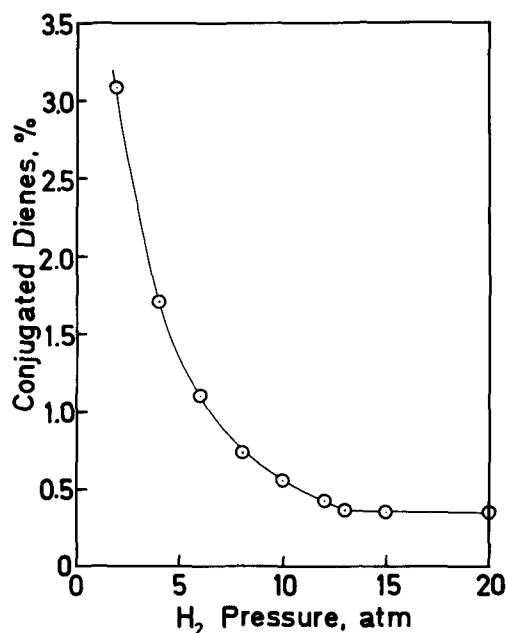


FIG. 4. Maximum percentage of conjugated dienes (UV absorption) vs. the hydrogen pressure (Cu-1106P, 0.5 wt % Cu in the oil, and 185 C).

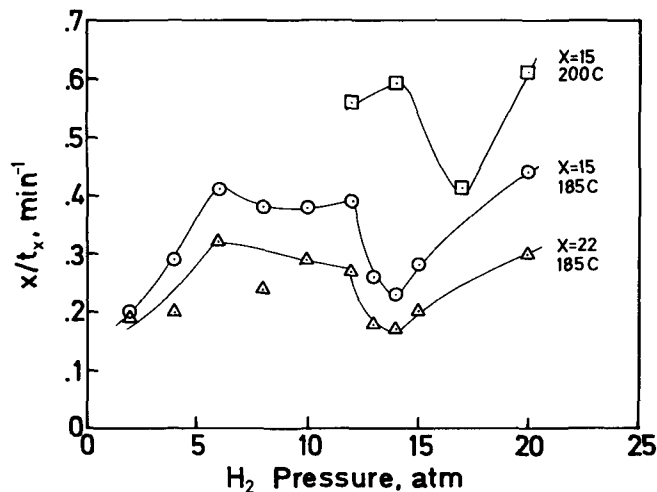


FIG. 5. Effect of hydrogen pressure on the mean rate of reaction in the hydrogenation of soybean oil (Cu-1106P, 0.05 wt % Cu in the oil, and 185 C).

13 atm.

The rate maximum at 6 atm is ascribable to the activity of $\text{Cu}/\text{Cu}^{\text{I}}$ combination (8). The contribution of the oxidic phase decreases with pressure. Judging from the accumulation of conjugated dienes, the oxidic surface makes a contribution up to a pressure of ca. 13 atm.

The Influence of Hydrogen Pressure on Selectivity

The simplified reaction model normally used for the calculation of the selectivity towards the linolenate component presupposes consecutive first order reactions, Trienes \rightarrow Dienes \rightarrow Monoenes. Here the selectivity S_{LN} towards the linolenate of soybean oil in hydrogenation at different pressures has been calculated from the GLC composition according to the program given by Butterfield et al. (11). The values given here correspond to an iodine value drop of 15 units, and the hydrogenation runs are the same as those represented in Figure 5 (Fig. 6).

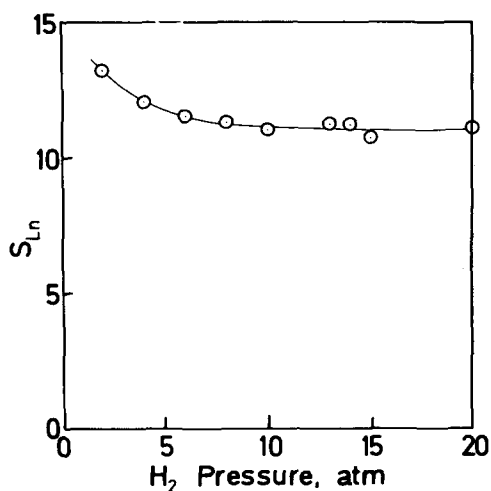


FIG. 6. Effect of hydrogen pressure on the selectivity S_{L_n} in the hydrogenation of soybean oil (Cu-1106P, 0.05 wt % Cu in the oil, and 185 C).

The variations between the different levels of hydrogen pressure are small. However, from a mechanistic point of view, the conclusions of Vigneron et al. (5) concerning hydrogenation below 5 atm are confirmed. Due to the relatively low hydrogen coverage of the catalyst surface, the triene molecules are desorbed to a greater extent after the first step of hydrogen addition.

The Course of Reactions at the Catalyst Surface

Catalytic activity requires the ability to adsorb fatty molecules and the ability to activate hydrogen molecules present in the oil. The accumulation of conjugated dienes in the oil indicates that fatty molecules are adsorbed at the surface of the catalyst but, due to a hydrogen shortage, the hydrogenation reaction cannot be completed.

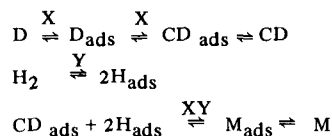
To judge from the accumulation of conjugated dienes, the conditions of adsorbing unsaturated fatty molecules are most advantageous at an oxidized phase of copper. As the presence of hydrogen is necessary, it is difficult to decide whether activation by partial reduction of the original catalyst surface is necessary or not, even if it is most probable. The dissociative adsorption of hydrogen is thus the rate-determining step of the process during the period of high reaction rate. Consequently, the ability of the catalyst to adsorb is decisive for the rate of hydrogenation. Since the two hydrogen-consuming reactions compete for the hydrogen adsorbed at the surface of the catalyst, the active sites involved in the two reactions are assumed to be the same. Therefore, being extensively described in the literature, the reduction of copper(II)oxide may serve as a model for the reduction of the copper chromite catalyst.

The copper(II)oxide is reduced in three stages — induction, autocatalytic or acceleratory, and decay — and the reactions start on certain active nuclei (12). The reactions occur at the interface between the copper metal nuclei and the surrounding copper oxide phase. The hydrogen is presumed to chemisorb on the copper metal near the interface and to migrate to the interface (13), or to be adsorbed on copper atoms in contact with the oxide (12). The contact between the copper atoms and the oxide must be very close as acceleration of the reduction cannot be produced by stirring metal into the oxide or by placing metal as a layer on the oxide (12). The copper metal must be produced within the oxide phase by reduction or, for instance, by decomposition of copper(II)formate.

The model is in all probability applicable to the part of the chromite catalyst consisting of copper(II)oxide crystal-

lites and, in view of the close contact between copper atoms and adjacent oxide, even applicable to the rest of the catalyst. According to the model, the dissociative adsorption of hydrogen increases during the two periods of catalyst reduction. When the reduction is finished, the ability of the catalyst to dissociatively adsorb the hydrogen diminishes.

Thus, favorable conditions for adsorbing fatty molecules exist at an oxidized surface, perhaps activated by a limited reduction to copper metal (Surface X). Favorable conditions for dissociative adsorption of hydrogen exist at an oxide surface during reduction, i.e., when copper metal atoms are in close contact with adjacent oxide (Surface Y). The reaction of hydrogenation is shown in the following scheme:



Here D is a system of two methylene-interrupted double bonds, CD is a system of two conjugated double bonds, and M is a monoene.

Above 12 atm the contribution of the copper phases subjected to reduction is low and the hydrogenation occurs mainly over a surface of copper metal on chromic oxide. If the copper content of the chromite catalyst is not totally reduced to metal, a positive contribution to the catalytic activity is implied. Our previous work (8) has shown that ca. 5% of the copper content is chemically bonded to the chromic oxide even after a hydrogenation at 20 atm and 185 C for 120 min.

During the first minutes of a hydrogenation run, the percentage of conjugated dienes in the oil is high and the hydrogen coverage of the catalyst surface is low. If the shortage of hydrogen is too marked, the risk of side reactions cannot be excluded. In the hydrogenation of methyl esters with copper chromite catalyst and deuterium, Koritala and Selke (9) found that the initial hydrogenation products contained only normal hydrogen; i.e., hydrogen atoms were transferred from other molecules to the molecules undergoing reduction. They proposed that hydrogen atoms of the dienes are first exchanged for deuterium atoms and then the hydrogen atoms are added to other diene molecules, which are hydrogenated. However, as far as we can see, this result would also imply that a step of self-hydrogenation is involved in the initial course of the hydrogenation process. Due to a low degree of hydrogen dissociation, hydrogen atoms temporarily bonded to the catalyst surface as a result of the adsorption of fatty molecules are added to other fatty molecules, which are hydrogenated. Such a hydrogen transfer was observed by Floyd et al. (14) on heating linolenic acid and its methyl esters in the presence of palladium. The donor molecules are hydrogenated in a consecutive step.

The dissociative adsorption of hydrogen is the rate-determining step during periods of high catalytic activity. However, owing to the connection between the catalyst reduction and the activity, the effect of a relative hydrogen shortage on the rate of hydrogenation may be only partially eliminated by an increase of pressure within the pressure range of a normal industrial fat hydrogenation converter.

The question concerning the most active oxidation state of copper has no simple answer. According to ESCA analyses of used copper chromite catalyst (8), all Cu^{II} ions are reduced within a few minutes of the process. Thus, the most active surface contains only Cu^I and Cu^D ions. The primary adsorption of the fatty molecules occurs at the oxide part of the surface, while hydrogen is adsorbed by the part with predominantly metallic properties. The

function of hydrogen adsorption is common for any hydrogenation system using a copper catalyst. The adsorption of the molecules subjected to reduction may vary, however, depending on the structure of the molecules.

The most ideal copper catalyst for fat hydrogenation, based on our experiences with the copper chromite catalyst, seems to consist of small copper metal crystallites partially covering a layer of oxidic copper which is resistant to further reduction and from which the metallic copper has been formed.

Concerning copper chromite catalyst in the pressure range below 14 atm, maximum rate of hydrogenation is obtained with fresh catalyst at 6 atm in the laboratory autoclave. If the difference of hydrogen transfer gas/liquid is regarded, the corresponding pressure level of an industrial converter with a volumetric mass transfer coefficient $k_a = 0.05 \text{ sec}^{-1}$ is calculated to ca. 8 atm.

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