Hydrogenation of Unsaturated Fatty Acids to Unsaturated Fatty Alcohols: I. Study of Cu and Cd Oleates as Catalysts

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Abstract

The catalyst system containing copper and cadmium oleates as used in selective hydrogenations was analyzed. The reddish brown reaction mixture as such and after precipitation by alcohol was subjected to polarographic, spectroscopic, x-ray and electron-microscopic analysis. The conclusion drawn was that the mixture is a heterogeneous system. From an electron micrograph it was observed that the average particle size is 48 Å. It was also possible to determine the mean degree of oxidation of copper in the precipitate, the results indicating that the copper is in its metallic state. Cadmium is present as cadmiumoleate, which stabilizes the copper colloid during the reaction.

Introduction

Unsaturated fatty alcohols can be produced from unsaturated fatty acids by high pressure hydrogenation. Effective catalysts are Adkins type systems with which a certain selectivity is possible if a co-catalyst such as Cd is added as oxide, carbonate or soap—is introduced during preparation of the copper and chromium oxide catalyst. Japanese authors also report the use of catalysts based on Zn (1). As to the conservation of the double bond during the reduction of oleic acid, the highest selectivity is obtained by using copper and cadmium soaps as catalysts (2). In view of the interesting properties of the catalyst a study of this hydrogenation process was undertaken at the Delft University of Technology. A hypothesis was finally put forward in which the active catalyst was copper hydride, CuH (3). This hydride would homogeneously reduce the acid to the corresponding unsaturated alcohol by the formation of a complex.

These studies have been continued and now result in more detailed information on the catalyst system. The kinetics of the hydrogenation with this and other catalyst systems will be dealt with in further papers.

Experimental Procedures

Preparation of the Samples

The reactions were carried out in a rocking autoclave which is represented diagrammatically in Figure 1. Hydrogenation takes place in vessel B at 250 C and 250 atm. of hydrogen. Periodic sampling is effected through tube D in such a way that the samples collected in vessel C are immediately cooled and passes out of the autoclave in an atmosphere of N_2 to avoid oxidation.

The acid-soap mixture to be hydrogenated is prepared by adding the desired amount of copper acetate and cadmium acetate to the oleic acid and heating on a water bath in a vacuum of 1 to 5 mm Hg for about 2 hr. This mixture is green at the start but passes out of the autoclave with a reddish brown colour. The reaction product contains some dark particles. By the addition of oxygen-free ethyl alcohol a material of a dark-brown color is precipitated. The precipitate is filtered and thoroughly washed with oxygen-free alcohol. After evaporation of the alcohol in vacuum a black powder remains.

Analysis of the Reaction Product

Polarographic Analysis. After destruction of the organic material the amount of Cu and Cd in the black powder was determined by means of polarography, using a dropping mercury electrode. The powder consists mainly of copper, only 0.2% to 0.5% of Cd being found. On the other hand in the alcoholic filtrate, no copper was found, but only cadmium.

X-Ray Analysis. In order to obtain an x-ray diffraction pattern of a sample from the autoclave the Debye-Scherrer diagram of a Straumanis photo from a Philips camera was used. The photographs were taken with the Cu-Kαbeam, the β-radiation being absorbed by a Ni screen. As cadmium was present as one of the components in the sample, an aluminum folio was interposed between the film and the x-ray source to diminish the effect of fluorescence. The exposure time was 2 hr for solids and 4 hr for solutions.

The samples to be analyzed were handled in a glovebox, which was introduced into a capillary tube, after which the two ends were sealed.

A Debye-Scherrer diagram of the reddish brown solution at different Cu and Cd concentrations and at different reaction times indicate only the presence of metallic copper. The strongest lines obtained in solution could only be classified as medium (see Table I). From Table I it can be seen that the copper line at Θ between 21 and 22.5° is very broad, indicating the presence of very small particles. The same is to be observed in the reaction product precipitated by alcohol, which shows exactly the same pattern as the solution. Cd oleate, Cu oleate, oleic acid and a mixture of these components, resulted only

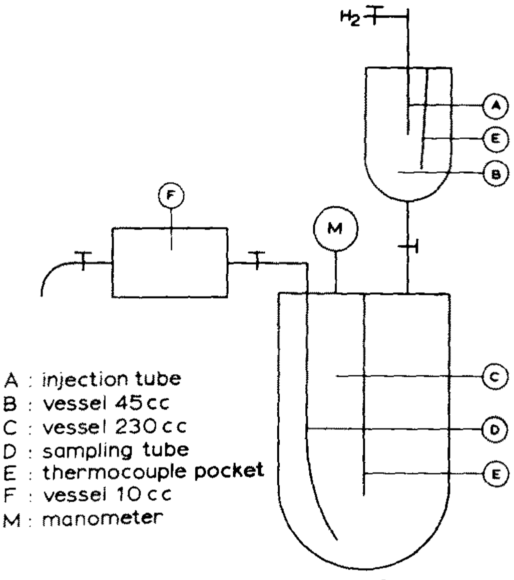

FIG. 1. High-Pressure autoclave.

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TABLE I

Diffraction Patterns of CuH, Reaction Product Solution (r.pr.s.) and Precipitate
For CuH (5): a = 2.89 ± 0.03 A, c = 4.63 ± 0.05 A; for Cu (14): a = 3.615 A

hkl	θ CuH calc.	θ (p)[a]	I	θ Cu calc.	θ (r)[b]	I	θ (t)[c]	I	θ (v)[d]	I	θ (z)[e]	I
100	17°52′	17°51′	m[f]	Not present	Not present		Not present		Not present		Not present	
001	19°27′	19°30′	m									
101	20°25′	20°15′ 20°30′	s[g]									
102	26°53′	26°54′	w[h]									
110	32°04′	32°01′	w									
103	36°01′	36°01′	m									
110(2)	37°54′	38°0′	w									
112	38°51′	38°54′	m									
200	39°30′	39°42′	w									
111		21°42′	m	21°42′	21°42′	m	21°0′ 22°30′	s	21°15′ 22°0′	m	21°15′ 22°0′	s
200		25°12′	w	25°12′	25°12′	w	25°12′	w	25°12′	w	25°12′	w
220		37°18′	w	37°18′	37°18′	w	37°18′	w	37°18′	w	37°18′	m
311		45°12′	w	45°12′	45°12′	w	45°12′	w	45°12′	w	45°12′	w
222		n.p.[i]	....	47°42′	n.p.	....	n.p.	....	n.p.	....	n.p.	....
400		n.p.	....	58°48′	n.p.	....	n.p.	....	n.p.	....	n.p.	....
331		68°52′	w	69°0′	68°57′	w	n.p.	....	68°57′	w	68°58′	w
420		72°45′	w	72°48′	72°46′	w	n.p.	....	72°46′	w	72°48′	w
	Unidentified lines	10°36′	w							Cu₂O	15°0′	w
		14°18′	w							Cu₂O	18°16′	w
		23°48′	w							Cu₂O	30°54′	w
		28°0′	w									

[a] (p) CuH prepared according to (5).
[b] (r) r.pr.s. of 28.6 mole % $CuOl_2$ and 14.3 mole % $CdOl_2$ in oleic acid, heated under an initial pressure of hydrogen of 190 atm. up to 250 C.
[c] (t) Same as (r), but Cu/Cd: 5/2.5 mole % and 30 min. at 250 C.
[d] (v) Same as (r), but Cu/Cd: 40/20 mole %.
[e] (z) Powder obtained by alcoholic precipitation of the reaction product solution.
[f] m—medium; [g] s—strong; [h] w—weak; [i] n.p.—not present.

in a very broad diffuse oleate ring, which appeared in all photos, of a 2 ⊖ value of 18–21°, which does not overlap CuH, Cu and its oxides or Cd, its oxides and $Cd(OH)_2$.

Determination of the Mean Oxidation Degree of Copper. As it did not prove possible to differentiate quantitatively by chemical analysis between the present oxidation states of copper in the reaction product, the mean oxidation degree was determined.

A method described by C. Okkerse et al. (4) was used for this purpose by making use of the equilibrium:

$$Cu^{+2} + Cu^{\circ} \rightleftarrows 2Cu^{+}$$

which is established if a system containing the three oxidation states of copper, Cu^{II}, Cu^{I} and Cu°, comes into contact with water. This equilibrium is shifted to the left in a 4N sulfuric acid solution and to the right in a 4N hydrochloric acid solution. A mean oxidation degree value, defined as x in CuO_x, can be determined by:

$$x = 1 - \frac{\text{\% copper as calculated from permanganometry}}{\text{\% total copper}}.$$

The value of x varies from 0 to 1; the lower the value of x, the greater the amount of reduced copper. To determine the value of x, samples were taken at different stages of the reaction, two at a time. One was kept in the glove-box and the other was left to be oxidized by the air, after which the total amount of copper was determined.

TABLE II

Mean Oxidation Degree of Copper in the Sample

Sampling time	% Cu°	% Total Cu	X
15 min	$96.4 \cdot 10^{-2}$	$97.3 \cdot 10^{-2}$	0.009
30 min	$96.6 \cdot 10^{-2}$	$97.2 \cdot 10^{-2}$	0.006
45 min	$96.6 \cdot 10^{-2}$	$97.3 \cdot 10^{-2}$	0.007
60 min	$96.5 \cdot 10^{-2}$	$97.3 \cdot 10^{-2}$	0.008
		medium value	0.0075

The sample kept in the glove-box was precipitated by alcohol and filtered. The dried precipitate was treated with an oxygen-free 2N-sulfuric acid solution at room temperature and stirred until the solid material was suspended. A ferric ammonium sulfate solution was added to the suspension, whereupon the whole was taken out of the glove-box and boiled for 1 hr so as to oxidize Cu° to Cu^{2+};

$$Cu^{\circ} + 2Fe^{3+} \rightleftarrows Cu^{2+} + 2Fe^{2+}.$$

The ferro ions formed were titrated with a 0.1 N $KMnO_4$ solution.

The total amount of copper was determined by treating the reaction product with a 2 N HCl solution; the greenish water layer was separated from the oil by extracting the latter with ether, both layers being completely homogeneous and clear. A 10% solution of KI was added to the water layer and the excess back-titrated with a 0.1 N thiosulfate solution.

It was observed that in boiling the acid-treated solution with the ferric salt under nitrogen the same results were obtained as if it has been boiled in the atmosphere. Cadmium did not interfere in the determination of copper, nor did oleic acid.

The results are set forth in Table II. The sampling time was taken at a reaction temperature of 250 C and a pressure of 200 atm of H_2. These conditions were kept constant throughout the experiment.

The reproducibility of these results was 2% to 3%. When higher percentages of copper were used, the x-values were the same within the error limit.

From the results set forth in Table III it is evident that Cu° is the oxidation state in which copper is present in the reaction product. That the value of x is not exactly nil, can be explained by traces of oxygen which came into contact with the sample during manipulation notwithstanding the extreme care taken.

When the mean oxidation degree of copper in CuH prepared by the Wurtz method (5) was determined, it was found that this copper consisted of Cu^{+}.

Tyndall Effect. Careful examination of the samples of the reddish brown reaction product diluted to

TABLE III

Hydrogenation of Oleic Acid With the Addition of Variant Copper Compounds. Experiments 1,2,4 and 5 were Carried Out in a Paraffin Solvent (6)

No.	Additives	Reaction time	Conversion to alcohol	Preservation of the double bond
1	0.16 g[a]	60 min	60%	50%
2	0.16 g[a] + 0.8 g $CdOl_2$	60 min	60%	100%
3	filtrate[c]	60 min	No reaction	
4	0.2 g CuH[b]	120 min	No reaction	
5	0.5 g CuH[b] + 2.4 g $CdOl_2$	20 min	No reaction	

[a] Precipitate obtained from the reaction product.
[b] According to (5).
[c] Alcoholic filtrate obtained as specified above.

50% with a paraffin mixture by an ultramicroscope with immersion objective showed a Tyndall effect.

Electron Microscopy. An electron micrograph of an embedded reaction product precipitated by alcohol showed particles of an average size of 48 Å (Fig. 2). Because of the good dispersion of the particles, probably due to dissolution of cadmium oleate and oleic acid in the resin, it was presumed that this is the size of the primary particles. The agglomerates are visible as dark patches.

Spectroscopy. Infrared spectroscopy of the dry powder pressed with KBr into a pellet or dissolved in a paraffin mixture, showed a spectrum corresponding to an oleate. The same can be said of the ultra-violet spectroscopical results.

Discussion

From the experiments it is clear that: not only copper is present in the powder sample of the precipitated reaction product but small amounts of cadmium as well; the powder sample contains oleate; the mean oxidation degree of the copper in the powder sample is 0.0075, indicating the presence of Cu° as the major component; no copper, only cadmium is present in the alcoholic filtrate sample of the reaction product; only Cu° lines were found in an x-ray diagram of the reaction product solution and powder sample; a Tyndall effect was observed in the reaction product solution. Further: no proton resonance signal or any signal for unpaired spin resonance was observed either in the solution or in the powder sample in cases where NMR and ESR investigation methods were employed. The powder sample is soluble in *n*-paraffins, ether, benzene, and is not soluble in oleic acid, alcohol and water at room temperature.

By analyzing these results it may be concluded that copper is present as the metal. The broadening of the x-ray diffraction pattern indicates particles which are very small, and the observation of the Tyndall effect may be an indication of particle size in the range of colloids.

As cadmium has not been observed as a metal in any x-ray diagram, whereas spectroscopy indentifies an oleate, it seems reasonable to conclude that cadmium is not reduced in the reaction and remains as cadmium oleate.

Experiments Leading to Final Conclusions

In order to test the reducing capacities of the dried powder a series of hydrogenations of oleic acid were carried out at 250 C and 200 atm. in which a paraffin mixture was previously saturated with H_2 at 250 C and 250 atm. for 2 hr in such a way that the substrate was immediately hydrogenated under reaction conditions. The amount of H_2 dissolved in the alkanes is more than sufficient to hydrogenate the oleic acid.

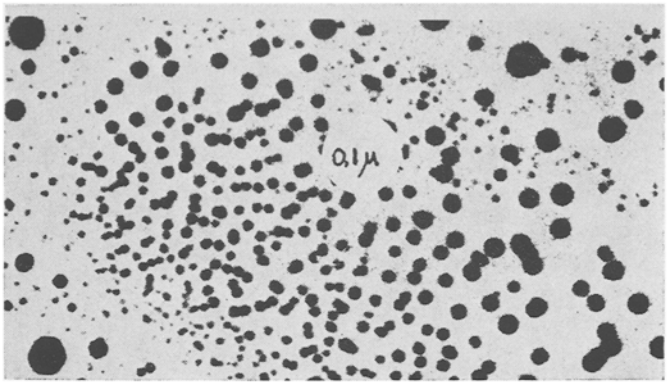

FIG. 2. Electron micrograph of the precipitated reaction product.

It also proved expedient to prepare CuH and to test its reducing activities towards an acid. The alcoholic filtrate (evaporated in a vacuum at room temperature) was also hydrogenated. The results are shown in Table III.

From these experiments some interesting features may be observed. In the first place the dark powder obtained from the reaction product is the active hydrogenating part of the catalyst, but a selective hydrogenation requires the presence of cadmium oleate. Only a small amount of this Cd-soap is present in the precipitate, which is not sufficient to carry out the hydrogenation selectively. In cases 1 and 2 the samples were reddish brown, but in case 1 the solution was turbid and in 2 completely homogeneous. With CuH the samples do not acquire the reddish brown color and there is no conversion.

It is now concluded that a copper sol is the active part of the catalyst system which effects hydrogenation. Cadmium oleate acts as a stabilizer for the colloid system. It is known that high-molecular acids and their metal soaps act as surface-active agents for the stabilization of colloid particles. The peptizing properties of the latter are even better. If the conditions, temperature, medium and sol-soap (or acid) concentration are suitable, the stabilization will be complete. The metallic part of the soap (or the polar part of the acid) is adsorbed to the sol particles, thus preventing agglomeration.

By the addition of alcohol, the polarity of the solution is increased and part of the metal soap is dispersed into it, only a monomolecular film of the stabilizer adsorbed to the particle being retained so that the particles can approach each other, but without entering each other's sphere of attraction, since they are protected by the monomolecular soap film. The unimolecular soap layer which is chemisorbed to the particles does not desorb when the concentration of the solution is reduced, this film remaining unimolecular in thickness (7).

The dry gel left after filtration of the alcoholic solution, may be redispersed by the addition of a paraffin, benzene or ether, forming a reddish brown solution.

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[Received October 2, 1968]