Selective Hydrogenation of Soybean Oil: V. A Novel Copper Catalyst With Excellent Re-use Properties

Abstract

A procedure for the preparation of highly active copper catalyst by chemisorption of copper-ammonia complex on silica gel is described. This catalyst was highly selective towards the reduction of linolenate in soybean oil. The catalyst was re-used four times with no loss in activity.

Silica gel adsorbs cations from ammoniacal solutions of certain metallic salts (1–4). The complex cations are so tightly bound to the gel surface that they cannot be washed out with water. In this report, we describe the preparation of highly selective catalysts with excellent re-use properties by the adsorption of ammoniacal copper ions on silica gel.

To 5 ml of an aqueous solution containing 1 g of copper nitrate ($Cu(NO_3)_2$ 3 H_2O), 1.8 ml of 30% ammonium hydroxide was added and the volume made up to 100 ml with distilled water. About 5 g of silica gel (MS-GEL:microspheroidal particles with average size 54 to 65 μ, surface area, 750 sq M/g; pore volume, 1.1 cc/g; average pore diameter, 59 A; supplied by Davison Chemical, W. R. Grace and Co.) was shaken with the copper-complex solution. The blue color disappeared from the solution instantly as the complex was adsorbed on the surface of the gel. The solution was left for 7 hr with occasional shaking. The gel containing copper-ammonia complex was separated by filtration, washed with distilled water, dried at 110 C, and calcined in air at 350 C for 2 hr. The catalyst was then added to 300 ml of refined and bleached soybean oil and hydrogenated in a Parr apparatus at 170 C and 30 psig hydrogen pressure. For comparative purposes both the hydrogenation procedure and the analytical methods were the same as those used in previous work (5). At the end of hydrogenation the oil and catalyst mixture was centrifuged. After pouring off the supernatant oil, the catalyst was transferred back for re-use into the hydrogenator by repeated washings with small amounts of a fresh batch of soybean oil.

Hydrogenation activity with this catalyst (Table I, Expt. 1) was as good as the previously reported copper-on-Cab-O-Sil catalyst (5). The new catalyst even slightly enhanced selectivity. It has been re-used four times with essentially no loss in activity (Expt. 2–5). Selectivity progressively decreased from 18 for the first hydrogenation to 13 for the fifth. The last selectivity compares favorably with the values of 11 to 13 achieved with commercial and laboratory-prepared copper chromites (6). Experiment 6 was carried out with a catalyst that was prepared by precipitating copper hydroxide on silica gel with ammonia, drying at 110 C and calcining at 350 C. Hydrogenation with this catalyst took 45 min and the same length of time was required for a similar catalyst precipitated with sodium hydroxide (5). Apparently the catalyst prepared from copper-ammonia complex is more active and selective than conventionally precipitated catalysts. The precipitated catalysts are dark grey after calcining. The new catalyst is green in color, changing to grey-black during hydrogenation. Upon standing, the catalyst regained its original green color.

Equally good catalyst was obtained when the gel was contacted with the complex for 15 min instead of 7 hr. There was some loss of activity when the contact time was increased to 24 hr or longer (hydrogenation time, 16 min). Doubling the amount of ammonia used to form the complex also decreased activity (reaction time 16 min). Silica gel is known to be slightly soluble even in weak alkaline solutions (2), and long periods of contact with ammoniacal solutions might possibly alter physical properties of the gel. Prolonged contact or the use of highly alkaline solutions should therefore be avoided.

Preparation of catalysts with other silica gels has been attempted. Under present experimental conditions most of them (ID-GEL; grades 56 and 952 GEL, Davison Chemical) did not adsorb all the complex copper ions even after prolonged standing. A few that did, exhibited markedly lower activity than the catalyst in Experiment 1 (922 GEL and Syloid 63 required 35 and 40 min, respectively).

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TABLE I

Hydrogenation of Soybean Oil With Copper Catalyst[a]

Experiment No.	Catalyst	Reaction time, min	IV drop	Per cent linolenate (alkali isomerization)	*Trans*, %	Selectivity K_{Le}/K_{Lo}
1	Silica gel-copper ammonia complex	12	13	0.6	8.3	18
2	Re-use from No. 1	11	14	0.6	8.9	15
3	Re-use from No. 2	12	14	0.6	9.4	15
4	Re-use from No. 3	13	14	0.6	8.8	14
5	Re-use from No. 4	13	14	0.8	8.2	13
6	Silica gel-copper hydroxide	45	12	0.9	7.5	14

[a] Total of 300 ml Oil at 170 C and 30 psig; Catalyst 0.3 g calculated as copper oxide.

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Scanning Electron Microscopy of Soybean Protein Bodies

Abstract

Protein bodies prepared from defatted soybean flour contained numerous spherical particles 1–3 μ in diameter, plus amorphous material, when examined in a scanning electron microscope. Full-fat and defatted soybean flours contained particles 1–10 μ in diameter. The larger protein bodies apparently disrupted during isolation. The scanning technique is a simple and rapid method for observing the effects of various treatments on subcellular seed particles of this size.

Many seed proteins are located in discrete cellular organelles called aleurone grains or protein bodies which have been isolated from several seeds. Characterization of protein bodies usually involves light and transmission electron microscopy. The scanning electron microscope has the advantage of a large depth of focus and direct viewing of samples without staining or sectioning. I have examined protein bodies isolated from mature soybeans and found, for the first time, that these materials are readily observed with the scanning electron microscope which should be useful in studies of the effects of grinding, defatting, and drying conditions on integrity of protein bodies.

Kanrich variety soybeans were cracked, dehulled and ground in an Alpine 160Z Kolleplex pin mill. The resulting meal was defatted at room temperature with pentane-hexane, air-dried, and material passing through a 325-mesh sieve was used to isolate the protein bodies by sucrose density gradient centrifugation at 25 C as described by Tombs (1). The sucrose solution containing the protein body fraction was diluted with distilled water, centrifuged, the protein bodies washed two to three times with water to remove sucrose, and finally dried in the centrifuge tube in a vacuum desiccator or freeze-dried. The protein body samples contained 82–83% protein (nitrogen X 5.8) in good agreement with values reported by Tombs (1) for his unfractionated preparations.

Ultracentrifugal analysis of the proteins in the protein body preparations confirmed that these are the storage sites of the major soybean proteins. Analyses in standard buffer (2) revealed 2S, 7S, 11S, and 15S components similar to those observed in the water-

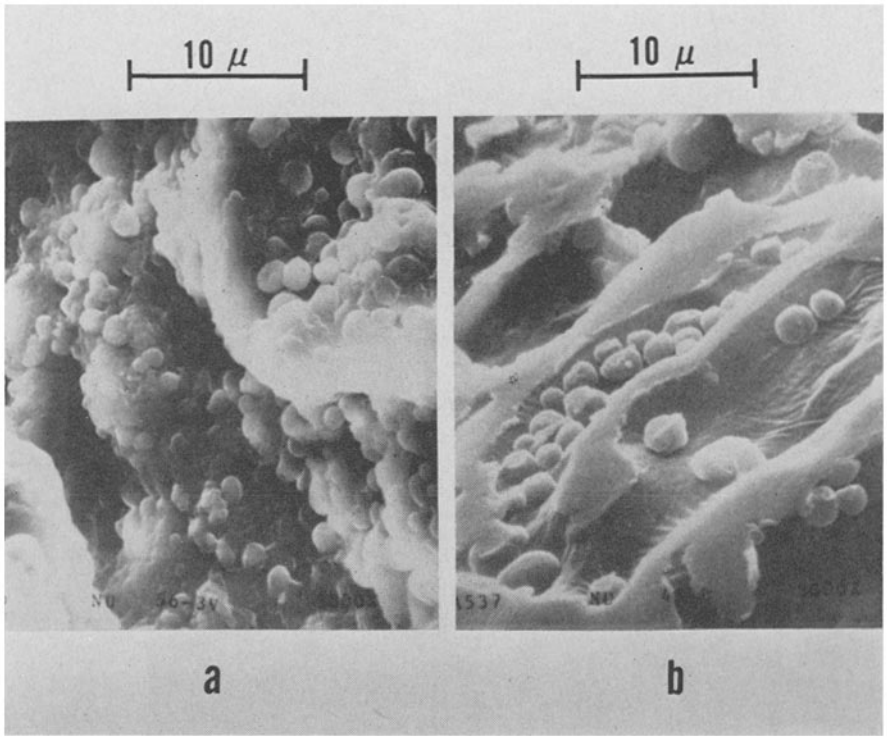

FIG. 1. Scanning electron micrograph of (a) soybean protein bodies and (b) pellet fraction obtained by sucrose density gradient centrifugation (× 3000). The samples were sprinkled onto a specimen holder covered with double-coated cellulose adhesive tape, coated with gold and then examined in a Stereoscan Mark II scanning electron microscope (Cambridge Instrument Co., Ltd., London, England).