Selective Hydrogenation of Soybean Oil. III. Copper-Exchanged Molecular Sieves and Other Supported Catalysts[1]

SAMBASIVARAO KORITALA, Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

Abstract

Copper-chromium catalysts promote selective reduction of linolenyl groups in soybean oil. Since commercially available catalysts possess only moderate activity, more active catalysts were sought. Copper was dispersed on high-surface-area supports, such as silica, alumina, and molecular sieves. These catalysts had varying activities. Precipitation of copper on Cab-O-Sil, a pure form of silica with a large external surface area, gave the most active catalyst. Selectivity ratios (K_{Le}/K_{Lo}) for the hydrogenation of soybean oil with these catalysts varied from 4 to 16; a copper-on-Cab-O-Sil catalyst exhibited the greatest selectivity. Improved selectivity and activity were observed when some supports were treated with hydrochloric acid. For example, with a copper-on-Celite catalyst, soybean oil was hydrogenated in 165 min and gave a selectivity ratio of 5.9. Hydrochloric acid treatment of Celite improved the selectivity to 9.9 and reduced hydrogenation time to 54 min. To ensure maximum activity of some of these catalysts, soybean oil should be more thoroughly bleached than is customarily done for nickel hydrogenation. A commercially refined and bleached soybean oil was hydrogenated with a copper-on-Cab-O-Sil catalyst in 18 min. The same oil, re-refined in the laboratory, was reduced in 11.5 min and had the same selectivity ratio of 15.

Introduction

COPPER-CHROMIUM CATALYSTS are useful because of their selectivity for removing linolenyl groups in soybean oil. Since commercial and laboratory-precipitated catalysts exhibit only moderate activity (1), more active catalysts were sought. In the absence of chromium, copper can function as a catalyst if exchanged on a molecular sieve (1). This investigation reports the preparation and performance of copper catalysts prepared on several supports such as silica, alumina, and molecular sieves.

Experimental Procedures

Catalysts were prepared in three different ways. The following examples illustrate the general procedures.

Copper-Exchanged Molecular Sieves. About 3 g of Linde molecular sieve 13X was stirred in 30 ml of an aqueous solution containing 2 g of copper nitrate. After exactly 1 hr the copper-exchanged molecular sieve (Cu:13X) was separated by filtration, washed thoroughly with distilled water, and dried at 100C. Analysis showed that Cu:13X contains 9.4% copper. This catalyst was then treated in two different ways. First, the Cu:13X was suspended in 20 ml of water, and 10 ml of a 5% sodium borohydride solution was added with stirring. The resulting product was separated by filtration, washed with distilled water, and dried (Cu:13X–$NaBH_4$). It was then heated to 350C for 2 hr before use. Alternatively Cu:13X was stirred with 30 ml of a 10% sodium carbonate solution for 0.5 hr. The product was filtered, washed, dried (Cu:13X–Na_2CO_3), and heated to 350C for 2 hr before use. Other catalysts were similarly prepared with 3A, 4A, 5A, 10X, and SK40 (Y) Linde molecular sieves.

Catalysts were also prepared by incorporating copper into sieves according to the procedure of Weisz et al. (2). To 3.7 g of sodium aluminate in 15 ml of water, 2 g of copper nitrate in 10 ml of water was added, followed by 7.2 g of sodium silicate in 35 ml of water. An additional 50 ml of water was added, and the whole mixture was refluxed while stirring for 7 hr. The resulting precipitate was separated by filtration, washed with distilled water, and dried. The catalyst (Cu in sieve $SiO_2/Al_2O_3 = 1.2$) was heated to 350C for 2 hr before use. Another catalyst was similarly prepared with a silica-to-alumina ratio of 2.5. The results of hydrogenation with these catalysts at two different temperatures are given in Tables I and II.

Coprecipitated Catalysts. To a stirred solution of 2 g of copper nitrate in 30 ml of water, 1.76 g of sodium silicate in 15 ml water was added. The resulting blue-green precipitate was separated by filtration, washed with distilled water, and dried. The ground powder was heated to 350C for 2 hr before use. Another catalyst was similarly prepared with sodium aluminate.

Supported Catalysts. These catalysts were prepared by precipitating copper on the support with the addition of stoichiometric amounts of either sodium carbonate or hydroxide. To 50 ml of aqueous solution containing 1 g of copper nitrate, 2.5 g Cab-O-Sil was added. The support was kept in suspension by vigorous stirring while about 439 mg of sodium carbonate in 10 ml of water was slowly added. The precipitate was separated, washed with distilled water, and dried. It was ground to a fine powder and heated to 350C for 2 hr before use. Catalysts were also similarly prepared with Aerosil 2491–380 (Degussa, Kearny, N.J.) and Santocel-62 (Monsanto, St. Louis, Mo.). All other supported catalysts were prepared with 3 g

TABLE I

Hydrogenation of Soybean Oil with Copper-Exchanged Molecular Sieve Catalysts (300 ml oil at 200C and 30 psi)

Expt. No.	Catalyst	Reaction time, min	IV Drop (GLC)	% Linolenate (alkali isomerization)	*trans*, %	Selectivity (K_{Le}/K_{Lo})
1	Cu:3A–K_2CO_3	37	15.0	2.1	9.8	5.0
2	Cu:4A–Na_2CO_3	19	10.3	1.4	7.2	10.9
3	Cu:4A–$NaBH_4$	32	14.2	1.5	9.5	7.2
4	Cu:5A–Na_2CO_3	157	12.6	3.1	10.0	4.3
5	Cu:5A–$NaBH_4$	91	14.4	2.7	9.6	4.0
6	Cu:10X–Na_2CO_3	105	14.5	2.6	11.8	4.3
7	Cu:13X–$NaBH_4$ (0.13%)[a]	13	14.7	0.8	8.4	11.0
8	Cu:13X–Na_2CO_3 (0.13%)	24	14.8	1.0	9.9	9.1
9	Cu:SK40–Na_2CO_3	95	10.5	1.7	7.8	9.8

[a] Values in parentheses represent catalyst concentration expressed as g of copper oxide per 100 ml of soybean oil.

---

[1] Presented at the AOCS Meeting, Chicago, October 1967.

[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE II

Hydrogenation of Soybean Oil with Copper-Exchanged Molecular Sieve Catalysts (300 ml oil at 170C and 30 psi)

Expt. No.	Catalyst	Reaction time, min	IV Drop (GLC)	% Linolenate (alkali isomerization)	*trans*, %	Selectivity, (K_{Le}/K_{Lo})
10	Cu:4A–Na_2CO_3	60	12.8	0.9	8.8	11.1
11	Cu:13X–Na_2CO_3 (0.26%)[a]	49	13.0	1.4	9.1	8.6
12	4A–Na_2CO_3–$Cu(NO_3)_2$ (0.2%)	22	11.8	1.1	7.2	12.1
13	Cu:SK40–Na_2CO_3	37	12.2	1.0	9.1	10.7
14	Cu in sieve $\frac{SiO_2}{Al_2O_3} = 1.2$ (0.2%)	12	12.7	0.7	9.7	12.4
15	Cu in sieve $\frac{SiO_2}{Al_2O_3} = 1.2$ (0.1%)	45	12.8	0.8	9.3	12.2
16[b]	Cu in sieve $\frac{SiO_2}{Al_2O_3} = 1.2$ (0.1%)	28	10.7	1.3	6.6	12.1
17	Cu in sieve $\frac{SiO_2}{Al_2O_3} = 2.5$ (0.2%)	15	12.8	1.3	10.1	9.5

[a] Values in parentheses represent catalyst concentration expressed as g of copper oxide per 100 ml of soybean oil.

[b] Re-refined and bleached oil.

of support for 1 g of copper nitrate. These include Celite, Filtercel (Johns-Manville, New York, N.Y.); Silica 923, MS Gel, ID Gel, Syloids 63, 72, and 244 (Davison Chemical Division, W. R. Grace Company, Baltimore, Md.).

Silica and alumina supports were also prepared in the laboratory by bubbling carbon dioxide gas into sodium silicate and sodium aluminate solutions respectively. The resulting gels (SiO_2 or Al_2O_3) were washed with distilled water, dried, and crushed to pass through a 100-mesh screen. Some supports were treated overnight with concentrated hydrochloric acid with occasional stirring. They were then washed thoroughly with distilled water and dried. The analytical results for soybean oil, hydrogenated with coprecipitated and supported catalysts, are given in Tables III and IV.

The commercially refined and bleached oils (FFA 0.04%) contained 7.6 to 8.2% linolenic acid (IV 133 to 137). One batch of oil was re-refined and bleached in the laboratory. The second refining was accomplished by adding to the stirred oil the theoretical amount of 10% sodium hydroxide required to neutralize the free fatty acids (FFA). The formed soap was removed by vacuum filtration over a bed of Celite. By this treatment FFA was reduced to 0.01% or less. The re-refined oil was then bleached at 110–115C with 1% of Super Filtrol-activated carbon mixture (9:1). While the oil was being heated under agitation, nitrogen gas was bubbled through the oil. When the temperature reached 80C, a bleaching earth-carbon mixture was added and heating was continued. Fifteen minutes after reaching the desired temperature, the oil was cooled and filtered under vacuum. The FFA of the bleached oil increased to 0.04%. Bleaching was also performed under vacuum with 0.5% AOCS neutral bleaching earth. FFA did not increase (0.01% or less) with this procedure.

The hydrogenation apparatus and the analytical methods were described previously (1,3). All experiments were performed with 300 ml of oil and with the same speed of agitation of 1,700 rpm. Selectivity ratios (K_{Le}/K_{Lo}) were determined with a digital computer, based on a program written by Butterfield and Dutton (4).

Discussion

Selectivity ratios at 200C for the hydrogenation of soybean oil with all copper-exchanged molecular sieves which were tested varied between 4 and 11 (Table I). The most active catalysts made with 4A and 13X (Expt. 2 and 7) were also the most selective for the reduction of linolenate. Treatment with sodium carbonate instead of sodium borohydride gave a more active catalyst with 4A (Expt. 2 and 3) whereas the reverse was true with 13X (Expt. 7 and 8). The structure of molecular sieve 4A was destroyed when copper was exchanged for sodium (5). Also, although triglycerides are not expected to pass into the pores of a 3A molecular sieve, yet hydrogenation did take place with this catalyst (Expt. 1). Copper precipitated on the external surface by adding the metallic salt solution to an alkaline solution containing 4A (Expt. 12, Table II) gave an equally good catalyst. Apparently the catalytic activity of these catalysts (at least 3A and 4A) lay mostly on the external surface. Catalysts with 5A and 10X (Expt. 4–6, Table I) were the least active and selective. Their low activity was probably caused either by the low exchange of

TABLE III

Hydrogenation of Soybean Oil with Supported Copper Catalysts (300 ml oil at 170C and 30 psi; catalyst, 0.1% as copper oxide)

Expt. No.	Support	Precipitating agent	Reaction time, min	IV Drop (GLC)	% Linolenate (alkali isomerization)	*trans*, %	Selectivity (K_{Le}/K_{Lo})
18	Celite	NaOH	165	13.4	2.2	9.3	5.9
19	Washed Celite	NaOH	54	13.1	1.1	8.4	9.9
20	Filtercel	Na_2CO_3	115	7.9	2.7	6.4	7.7
21	Washed Filtercel	Na_2CO_3	40	10.3	2.0	6.1	11.3
22	Silica 923	NaOH	48	13.3	0.9	8.0	10.9
23	Washed Silica 923	NaOH	66	11.1	1.3	8.0	12.3
24	Washed Silica 923[a]	NaOH	54	14.9	0.9	7.7	11.6
25	MS Gel	NaOH	45	12.2	0.7	9.2	13.8
26	Washed MS Gel	NaOH	30	13.1	0.7	10.5	13.1
27	ID Gel	NaOH	30	13.3	0.7	8.7	12.6
28	Washed ID Gel	NaOH	25	12.0	0.9	10.0	12.0
29	Syloid 63	NaOH	28	13.7	0.6	9.9	13.1
30	Syloid 72	NaOH	32	13.8	0.6	9.7	14.3
31	Syloid 244	NaOH	33	13.7	0.8	9.2	13.2
32	Harshaw alumina[b]	Na_2CO_3	57	11.4	1.7	8.5	9.0
33	Al_2O_3	Na_2CO_3	54	15.4	0.6	7.6	14.2
34	SiO_2	NaOH	37	13.6	0.9	9.0	12.1
35	None	$NaAlO_2$[b]	64	13.0	1.3	10.1	9.2
36	None	Na_2SiO_3[b]	40	12.5	1.2	8.9	10.0
37	Raney copper[c]		21	11.9	1.4	7.6	8.6

[a] Treated with 1*N* hydrochloric acid.

[b] Catalyst concentration 0.2% expressed as g of copper oxide per 100 ml of oil.

[c] Catalyst concentration 1.0%.

TABLE IV

Hydrogenation of Soybean Oil with Supported Copper Catalysts
(300 ml at 170C and 30 psi; catalyst, 0.1% as copper oxide)

Expt. No.	Support	Precipitating agent	Reaction time, min	IV Drop (GLC)	% Linolenate (alkali isomerization)	*trans*, %	Selectivity (K_{Le}/K_{Lo})
38	Cab-o-Sil M5	Na_2CO_3	13	12.1	0.8	9.8	13.2
39	Catalyst from Expt. 38		25	11.7	0.8	10.0	12.7
40	Cab-o-Sil M5	Na_2CO_3	18	12.0	0.6	9.8	15.5
41[a]	Cab-o-Sil M5	Na_2CO_3	11.5	12.8	0.5	8.6	15.3
42[b]	Cab-o-Sil M5	Na_2CO_3	12.5	12.6	0.5	10.1	16.0
43[a]	Cab-o-Sil M5[c]	Na_2CO_3	16	13.0	0.6	9.1	13.9
44[a]	Cab-o-Sil M5	Na_4OH	55	11.4	1.4	7.2	11.4
45[a]	Santocel 62	Na_2CO_3	13	13.4	0.6	9.6	14.4
46	Cab-o-Sil EH5	Na_2CO_3	22	15.9	0.6	8.7	12.9
47[a]	Cab-o-Sil EH5	Na_2CO_3	18	12.6	0.6	11.0	15.2
48[a]	Cab-o-Sil EH5	Na_2CO_3	20	13.6	0.5	9.7	16.5
49[a]	Cab-o-Sil M5[d]	Na_2CO_3	18	11.0	1.1	7.2	13.2
50[a]	Aerosil[d]	Na_2CO_3	31	10.0	1.2	7.7	14.9
51[a]	Nickel catalyst[e]		2	15.1	3.8	10.8	2.1

[a] Re-refined and bleached oil.
[b] Vacuum-bleached with AOCS neutral bleach.
[c] 0.75 g of support.
[d] Catalyst concentration 0.05%; 45 psi.
[e] G-15 commercial nickel catalyst (Girdler catalysts, Chemetron Corporation, Louisville, Ky.) 0.04% Ni; 15 psi.

copper or by the presence of calcium which may have inhibited the reaction.

Both 4A and 13X copper catalysts active at 200C showed only moderate activity at 170C (Expt. 10 and 11, Table II). These catalysts probably require prior activation at the higher temperature. Better activity and selectivity were achieved with catalysts made by incorporating copper into molecular sieves while they were being crystallized (Expt. 14–17). The molecular sieve catalyst with the higher silica content gave lower selectivity. Experiments 15 and 16 were performed with two different oils, a commercial refined oil and a laboratory re-refined oil. It can be readily seen that treating the oils in the laboratory improved catalyst activity. This improvement was also true with other catalysts, as will be seen later. The most active catalyst (Expt. 14) promoted the hydrogenation of soybean oil in 12 min when 0.2% copper oxide was used. The most active commercial copper-chromium catalyst under the same conditions required 36 min (1). Thus a copper-in-sieve catalyst was three times more active.

The selectivity achieved with supported copper catalysts varied between 5.9 to 16.5 (Tables III and IV). Washing the supports before precipitating copper improved activity or selectivity, or both (Expt. 18–28). With Celite and Filtercel both selectivity and activity improved markedly. With Silica 923 there was only slight improvement in selectivity but not in activity. With MS and ID Gels, selectivity remained the same, but activity improved. Iron was extracted from the support during acid treatment. The increased activity of the catalysts after acid extraction of the supports was probably attributable to the removal of iron, which may be a catalytic inhibitor.

There does not seem to be any correlation between the activity of the catalyst and the surface area of the support. Among the Davison silica gels (Expt. 22–28), the one with the least surface area (ID Gel) had the greatest activity. The higher activity with the low surface support may have been caused by its large pores, through which triglycerides could diffuse in and out more freely. In spite of the large difference in surface area among the Syloids (300–800 sq m/g), the activity of the catalysts was nearly the same (Expt. 29–31). Laboratory-precipitated silica performed almost as well as the most active commercial silica (Expt. 27 and 34). Laboratory-precipitated alumina had greater selectivity and activity than commercial grade (Expt. 32 and 33).

Raney copper (Expt. 37) catalyzed the hydrogenation of soybean oil even though selectivity and activity were markedly lower than with some of the supported catalysts. This behavior raised the question as to the nature of the active form of copper in the catalysts. Connor et al. (6) maintained that the active agent in copper-chromium catalysts is copper in its divalent state and that, whenever copper is reduced to reddish metallic or monovalent copper, the catalyst is rather inactive. My experience was in accord with theirs, particularly with copper-exchanged molecular sieves 3A, 5A, and 10X and catalysts supported on Celite and Filtercel, which turned red during the reaction. In a recent study (7) it was claimed that the active agent in Cu-Mg-SiO_2 catalyst is in the metallic state. Opposing views on the nature of the active catalyst suggest that further work is required before any definitive conclusions can be reached.

By far the most active and selective catalysts were obtained with fumed silicas (Table IV), which are claimed to be the purest forms of silica available. All their surface area lies on their exterior, and they have no internal voids. Thus there will be no diffusion limitations, and all the copper precipitated on this support is readily available for the triglycerides.

Experiments 38 and 39 were performed with an original batch of oil. Some activity (but no selectivity) was lost during re-use of the catalyst. When a different batch of oil was used (Expt. 40) with the same catalyst, the time of hydrogenation increased considerably. Re-refining and bleaching this oil with either active or neutral bleaching earth (Expt. 41 and 42) improved activity considerably. It was therefore important to bleach the oil more thoroughly than is customarily done for nickel hydrogenation in order to achieve maximum activity with this catalyst. With EH5 Cab-O-Sil however there was no improvement in activity (Expt. 46–48). Even though EH5 Cab-O-Sil and Aerosil has about twice as large a surface area as M5 Cab-O-Sil, their activity was much lower (comparison between Expt. 41 and 48; 49 and 50). As little as 0.75 g of support for 1 g of copper nitrate gave a good catalyst even though the activity was slightly diminished (Expt. 43). Copper supported on Santocel also formed an active and selective catalyst (Expt. 45).

The precipitating agent seems to have a great effect on the activity of the catalyst. When ammonia was used to precipitate copper on Cab-O-Sil, a catalyst with poor activity and selectivity resulted (Expt. 44).

The most active copper catalyst was about nine times less active than a commercial nickel catalyst when the same amount of metal was employed (Expt. 49 and 51). However selectivity of a copper catalyst was much higher than with nickel. The most active copper-chromium catalyst hydrogenated soybean oil in 36 min when 0.2% copper oxide was used (1). The same reaction was complete in 11.5 min with Copper-on-Cab-Sil (Expt. 41) even though much less copper oxide was present.

With all catalysts prepared for and used in this study, about 7–12% *trans* isomers were formed during hydrogenation. Also 1–3% diene conjugation was produced; the higher temperature of hydrogenation favored the formation of conjugation. More than 75% of the original linoleate in soybean oil was retained in the hydrogenated products as measured by alkali isomerization.

ACKNOWLEDGMENT

Infrared analyses were performed by Miss Janina Nowakowska and Richard L. Hoffmann. The author is grateful to H. J. Dutton and J. C. Cowan for their counsel in the investigation.

REFERENCES

1. Koritala, S., and H. J. Dutton, JAOCS *43*, 556–558 (1966).
2. Weisz, P. B., V. J. Frilette, R. W. Maatman and E. B. Mower, J. Cataly. *1*, 307–312 (1962).
3. Koritala, S., and H. J. Dutton, JAOCS *43*, 86–89 (1966).
4. Butterfield, R. O., and H. J. Dutton, *Ibid. 44*, 549–550 (1967).
5. Breck, D. W., W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, J. Amer. Chem. Soc. *78*, 5963–5971 (1956).
6. Connor, R., K. Folkers and H. Adkins, Ibid. *54*, 1138–1145 (1932).
7. Okkerse, C., A. De Jonge, J. W. E. Coenen and A. Rozendaal, JAOCS *44*, 152–156 (1967).

[Received October 13, 1967]