quality salad oils, deep or French frying oils, and in highly polyunsaturated margarines. Although the yields will be lower for the sunflower planted later in the year, oil for the different uses can be obtained by merely selecting the season of the year that results in its having the desired fatty acid composition.

ACKNOWLEDGMENT

J.H. Lefiles provided technical assistance. R.L. Wilson provided statistical analyses.

REFERENCES

1. Canvin, D.T., Can. J. Bot. 43:63 (1965).
2. Robertson, J.A., J.K. Thomas and D. Burdick, J. Food Sci. 36: 873 (1971).
3. Robertson, J.A., W.H. Morrison, III, and R.L. Wilson, "Effects of Planting Location and Temperatures on the Oil Content and Fatty Acid Composition of Sunflower Seeds," USDA, SEA, Agricultural Research Results, ARR-S-3/, October 1979.
4. Unger, P.W., Agron. J. (in press).
5. Graves, C.R., J.R. Overton, T. McCutchen, B.N. Duck and J. Connell, "Production of Sunflowers in Tennessee," Bulletin 494, University of Tennessee Agric. Expt. Sta., Knoxville, TN, April 1972.
6. Robertson, J.A., and W.H. Morrison, III, JAOCS 56:961 (1979).
7. Robertson, J.A., G.W. Chapman and R.L. Wilson, Ibid. 55:266 (1978).
8. Keefer, G.D., J.E. McAllister, E.S. Uridge and B.W. Simpson, Aust. J. Exp. Agric. Anim. Husb. 16:417 (1976).
9. Robinson, R.G., Agron. J. 62:665 (1970).
10. Anderson, W.K., R.C.G. Smith and J.R.M. William, Field Crops Res. 1:141 (1978).
11. Robinson, R.G., Crop Sci. 11:635 (1971).

[Received November 10, 1980]

Selective Hydrogenation of Soybean Oil: XI. Trialkyl Silane-Activated Copper Catalysts

S. KORITALA, Northern Regional Research Center, Agricultural Research,
Science and Education Administration, U.S. Department of Agriculture,
Peoria, IL 61604

ABSTRACT

Addition of triethyl silane to copper stearate resulted in an active heterogenous catalyst for the hydrogenation of soybean oil. The linolenate selectivity of this catalyst (K_{Le}/K_{Lo} = 2.4 to 3.9) was much lower than that obtained with copper chromite (8.4). Unlike copper-chromite catalyst, triethyl silane-activated copper formed stearate during hydrogenation. Both silica and alumina increased catalyst activity. Linolenate selectivity improved slightly in the presence of alumina.

Previous investigators have shown that copper catalysts are, by far, the most selective for the hydrogenation of linolenate in soybean oil (1,2). However, the activity of these catalysts is much lower than that of commercial nickel catalyst (3). Copper catalysts of improved activity are obtained when copper is supported on high surface silica (4-6).

Tulupov reported that copper stearate catalyzes the homogeneous hydrogenation of cyclohexene in ethanol at room temperature (7). Later, Larsen and Chang (8) were unable to repeat the work. Copper oleate in admixture with cadmium oleate catalyzed the hydrogenolysis of oleic acid to oleyl alcohol (9). The active catalyst was reported to be heterogeneous with an average particle size of 4.8 nm.

In this laboratory, copper stearate by itself was found to hydrogenate soybean oil slowly. Addition of triethyl silane (TES) resulted in a heterogeneous catalyst with improved activity. In this report, the results of hydrogenation of soybean oil with the new catalyst system is described.

The preparation of the catalyst and hydrogenation procedure is briefly as follows. About 75 g commercially refined and bleached soybean oil, 0.37 g copper stearate (ICN Pharmaceuticals, Inc., Plainview, NY) and, when necessary, 0.37 g each of either Cab-O-Sil or Alon C (fumed silica or alumina from Cabot Corporation, Boston, MA) were heated in an Erlenmeyer flask equipped with a side arm, which was sealed with a serum cap, to 70 C under vacuum to remove any traces of moisture. The mixture was then magnetically stirred and kept under a blanket of nitrogen while 1 ml TES (Petrarch Systems, Inc., Levittown, PA) was injected through the serum cap. No visible reaction occurred at this temperature. The active catalyst is apparently formed at the temperature of the reaction. The whole mixture was then transferred under nitrogen pressure as quickly as possible into a 150-ml magnetically stirred, Magna-Dash autoclave which was electrically heated to 200 C under 10 psi nitrogen. Hydrogen (150 psi) was admitted from an external reservoir through a pressure regulator valve. Samples were removed at intervals for analyses by methods described previously (10).

The plot of log IV vs time (Fig. 1) showed that copper

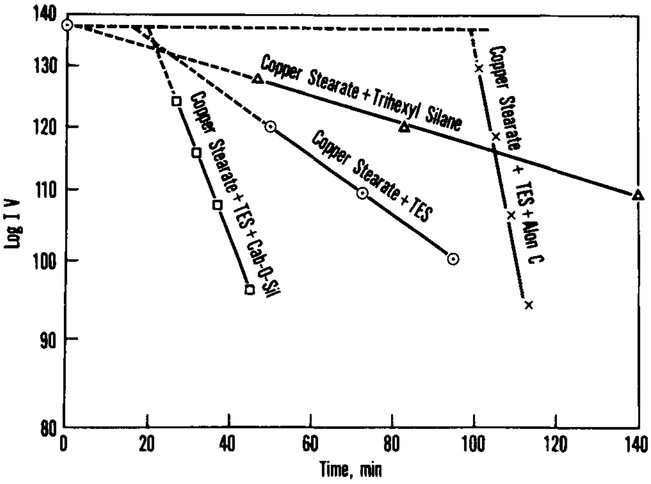

FIG. 1. Hydrogenation of soybean oil with trialkyl silane-activated copper catalysts (0.05% copper at 200 C and 150 psi).

TABLE I

Hydrogenation of Soybean Oil with Triethyl Silane (TES) Activated Copper Catalyst[a]

Catalyst	Reaction time (min)	Fatty acid composition[b]				IV calculated	% *trans* (% trans/ΔIV)	Selectivity	
		St	M	D	T			K_{Le}/K_{Lo}	K_{Lo}/K_{Ol}
None	–	3.9	21.1	56.7	8.1	137.5	–	–	–
A Copper stearate	330	4.7	32.6	47.5	5.0	123.4	12.3 (0.87)	2.0	8
B Copper stearate + TES	73	5.1	44.9	37.6	2.2	109.5	23.1 (0.83)	2.4	15
C Copper stearate + + Trihexyl silane	140	4.7	46.2	36.7	2.2	109.1	23.3 (0.82)	2.3	24
D Copper stearate + TES + Cab-o-sil	37	5.1	46.2	36.7	1.8	108.0	25.7 (0.87)	2.7	15
E Copper stearate + TES + Alon C	109	4.6	48.4	35.9	0.8	106.2	22.7 (0.73)	3.9	35
F Commercial copper chromite	270	4.0	32.7	51.9	1.4	121.7	11.2 (0.71)	8.4	∞

[a] 0.05% copper, 200 C; 150 psi.

[b] St = stearate; M = monoene; D = diene; T = triene.

stearate-TES catalyst has an induction period. Addition of alumina increased this induction period, but it remained essentially unchanged with silica. The negative slopes of these plots are proportional to the rate of reaction (11). The slopes for the hydrogenation with catalyst-containing silica and alumina were compared to that of copper stearate-TES catalyst. On this basis, silica and alumina increased the rate of reaction 3.5 and 6.8 fold, respectively. When trihexyl silane replaced TES, the activity was reduced by more than half.

Typical fatty acid compositions, selectivity ratios and percentage *trans*-isomer values are given in Table I. Copper stearate (A) by itself had very little catalytic activity. After 330 min of reaction, the iodine value (IV) dropped by only 14 units. Addition of TES (B) resulted in a more active catalyst which reduced the IV by 28 units in 73 min. Trihexyl silane (C) is not as effective as TES in activating copper stearate. TES-activated catalyst (B) had linolenate selectivity (K_{Le}/K_{Lo}) of 2.4. This is in marked contrast to the value of 8.4 obtained with copper-chromite (F) catalyst. The linoleate selectivity (K_{Lo}/K_{Ol}) is infinite with copper chromite (F), whereas copper stearate-TES (A) gave a value of 15. Addition of silica in the form of Cab-o-sil (C) had no effect on linolenate selectivity, but alumina (D) improved both linolenate and linoleate selectivities. A decrease in *trans*-isomers was observed with alumina as judged by the percentage of *trans* per unit iodine value drop.

To improve linolenate selectivity, hydrogenation was done at lower temperature (170 C) with 0.1% copper; however, no reaction occurred in 3-5 hr. Apparently, higher temperatures are required to activate the catalyst.

The catalyst systems of Table I are not as selective as copper chromite, but they are more active than the commercial copper chromite catalyst. For example, hydrogenation was successfully completed (73 min for 28 IV drop) with 0.05% copper (B) at 200 C and 150 psi. Copper-chromite catalyst required 270 min to drop the IV by 16 units. The reason for the lowered selectivity is probably due to the nature of the active catalyst species. The active species in copper-chromite catalyst is presumed to be divalent (12), and when it turns red the resulting monovalent or metallic copper is inactive for certain reactions. These catalysts are also reddish, indicating the metallic nature of the catalyst. Poor selectivity also resulted previously when a sodium borohydride-reduced copper catalyst (1) turned red during hydrogenation. Some of the catalysts of Table I may have potential industrial use for the selective hydrogenation of soybean oil.

REFERENCES

1. Koritala, S., and H.J. Dutton, JAOCS 43:86 (1966).
2. DeJonge, A., J.W.E. Coenen and C. Okkerse, Nature 206:573 (1965).
3. Koritala, S., JAOCS 45:197 (1968).
4. Koritala, S., Ibid. 47:106 (1970).
5. Koritala, S., Ibid. 49:83 (1972).
6. Koritala, S., Ibid. 54:267 (1977).
7. Tulupov, V.A., in "Homogeneous Hydrogenation," edited by B.R. James, Wiley, New York, NY, 1973, p. 384.
8. Larsen, J.W., and L.W. Chang, J. Org. Chem. 41:3332 (1976).
9. Richter, J.D., and P.J. Van Den Berg, Jaocs 46:155; 46:158 (1969).
10. Mounts, T.L., S. Koritala, J.P. Friedrich and H.J. Dutton, Ibid. 55:402 (1978).
11. Wisniak, J., and L.F. Albright, Ind. Eng. Chem. 53:375 (1961).
12. Connor, R., K. Folkers and H. Adkins, J. Am. Chem. Soc. 54:1138 (1932).

[Received January 26, 1981]