Selective Hydrogenation of Soybean Oil. VIII. Effect of Method of Preparation Upon the Activity of a Copper-Silica Catalyst[1]

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ABSTRACT AND SUMMARY

A copper-silica catalyst was prepared by adding copper nitrate solution to sodium silicate. The precipitated copper-silica catalyst was washed, dried, and heat-treated at high temperatures. The effect of preparational variables upon catalyst activity and selectivity for the hydrogenation of soybean oil was investigated. The optimum conditions were precipitation at 25 to 55 C, drying the catalyst by freeze drying, and heat treatment at 500 C. The catalyst obtained under these conditions is more than three times as active as a commercial copper-chromite catalyst.

INTRODUCTION

It was amply demonstrated that copper catalysts are by far the most selective for hydrogenating the linolenic acid in soybean and other vegetable oils (1-4). One serious drawback of commercially available copper-chromite catalysts is that they are much less active for hydrogenation than conventional nickel catalysts. Copper supported on high-surface silica formed a more active catalyst than commercial copper-chromite (5,6). However, because of the added cost of expensive supports, these catalysts may be uneconomical to use. Coprecipitated copper-silica catalysts are expected to be cheaper to produce, since the need for expensive supports is eliminated. We now report the method of preparing an active and selective catalyst.

EXPERIMENTAL PROCEDURES

Soybean Oil

Refined, bleached soybean oil [free fatty acids (FFA) 0.09%] was obtained from a commercial source. It was re-refined with theoretical amount of sodium hydroxide and then bleached with 0.5% Super Filtrol at 105-110 C under 0.5 mm vacuum. The re-refined and bleached oil had an FFA content of 0.01%.

Catalysts

To 50 ml of a well-stirred aqueous solution containing 4.388 g (0.0207 moles) of sodium silicate ($Na_2SiO_3 \cdot 5H_2O$) is added dropwise 5 g (0.0207 moles) of copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$] in 25 ml distilled water at room temperature. The copper-silica precipitate was washed three times by stirring in 400 ml distilled water each time and removing the supernatant after centrifugation. The washed precipitate was then dried at 110-115 C for 2 hr to yield 3.15 g. One-fifth of this catalyst (0.26 g copper assuming no losses during preparation) was heated in a furnace at 500 C for 2 hr and used for hydrogenation. Several variations were applied to this standard method of catalyst preparation to obtain different catalysts. The variations consisted of the temperature of precipitation, method of drying, and the temperature of heat treating the catalyst. Yet another method of preparation consisted of reverse addition, namely addition of sodium silicate to copper nitrate solution.

Hydrogenation

Hydrogenations were carried out in a Parr apparatus equipped with a gas dispersion agitator (7) running at 1700 rpm. The oil (270 g) and the catalyst (0.26 g copper) were added to the autoclave. flushed with nitrogen, and heated to 170 C. The bomb was then evacuated, flushed with hydrogen, and filled to 30 psi.The agitator was turned on to start the reaction. Hydrogen pressure inside the reactor was maintained constant at 30 psi by introducing hydrogen from an external reservoir tank through a pressure regulator valve. The extent of reaction was measured from the drop in pressure in the external reservoir tank. After the desired amount of reaction, the stirrer was turned off and the bomb was cooled. The oil was separated from the catalyst by filtration through Celite.

Analytical Methods

Methyl esters were prepared from triglycerides by transesterification with sodium methoxide catalyst. The percentage isolated *trans* was measured by infrared (IR) absorption at 10.36 μm of methyl esters and by comparison with methyl elaidate standard. Diene conjugation and percent linolenate were determined by the official AOCS method (8). Gas liquid chromatography (GLC) was performed with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless-steel columns packed with 15% ethylene glycol succinate methyl silicone polymer (EGSS-X) on Gas-Chrom P, 100-120 mesh and with flame ionization detectors. Peaks were electronically integrated with the aid of a digital computer. Fatty acid composition was computed from GLC and spectrophotometric analyses. From the composition of the initial and hydrogenated soybean oils, selectivity defined as the ratio of rate of reaction of linolenate (K_{Le}) over that of linoleate (K_{Lo}) was determined with a digital computer, based on a program written by Butterfield and Dutton (9).

RESULTS AND DISSCUSION

The results of selective hydrogenation of soybean oil with various experimental catalysts and with a commercial catalyst are given in Table I. The relative activity of the catalyst shown in the last column was calculated as iodine value drop per minute as compared to commercial copper-chromite catalyst. Coprecipitated copper-silica catalyst (No. 2) was more active than commercial copper chromite (No. 1). However, the selectivity of this catalyst was somewhat lower. When the coprecipitated catalyst was vacuum-dried (No. 3), both activity and selectivity improved. An even more active catalyst (No. 4) was formed when it was freeze dried. This catalyst was 3.4 times as active as the commercial catalyst.

The temperature at which precipitation was carried out has great influence on the activity of the catalyst (Nos. 4-7). Best catalyst was obtained in the temperature range of 25-55 C. Precipitation of 0 C gave a somewhat inferior catalyst, while precipitation at 100 C gave the poorest catalyst.

The temperature of activation also influenced catalyst activity (Nos. 4, 8-11). Best activity was observed for the catalyst that was heat activated at 500 C. Activity was slightly diminished when catalysts were heat treated at 425

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TABLE I

Effect of Method of Preparation on the Activity of Copper-Silica Catalyst[a]

Catalyst No.	Method of catalyst preparation	Reaction time (min)	IV drop	Linolenate (%)	Diene conjugation (%)	*trans* (%)	Selectivity, K_{Le}/K_{Lo}	Relative catalyst activity[b]
1	Commercial copper-chromite	59	15.7	0.6	1.3	10	14	1.00
2.	Precipitation 25 C, dried 110 C, heat treated 500 C	35	15.6	1.2	1.5	9	10	1.68
3	Precipitation 25 C, dried under vacuum 25 C, heat treated 500 C	23	14.7	1.0	1.7	9	13	2.40
4	Precipitation 25 C, freeze dried, heat treated 500 C	17	15.2	0.8	1.8	9	13	3.36
5	Precipitation 55 C, freeze dried, heat treated 500 C	17	15.4	0.7	1.8	8	14	3.41
6	Precipitation 0 C, freeze dried, heat treated 500 C	29	15.0	0.9	1.6	8	13	1.94
7	Precipitation 100 C, freeze dried, heat treated 500 C	41	14.7	0.9	1.5	8	13	1.35
8	Precipitation 25 C, freeze dried, heat treated 350 C	30	15.0	0.9	1.2	8	13	1.88
9	Precipitation 25 C, freeze dried, heat treated 425 C	20	15.5	0.8	1.7	8	13	2.91
10	Precipitation 25 C, freeze dried, heat treated 575 C	19	15.5	0.7	1.7	9	14	3.07
11	Precipitation 25 C, freeze dried, heat treated 650 C	50	15.0	1.1	1.4	8	11	1.11
12	Precipitation 25 C (reverse addition), freeze dried, heat treated 500 C	22	14.9	0.9	1.7	8	13	2.55

[a] Oil (270 g), catalyst containing 0.26 g copper at 170 C, hydrogen pressure 30 psig, and agitation 1700 rpm.

[b] IV drop/min relative to commercial copper chromite catalyst.

and 575 C. Catalyst activity diminished considerably when catalysts were heat treated at 350 or 650 C. Reverse addition of sodium silicate to copper nitrate resulted in a slight loss of activity (No. 12).

The various methods of preparation of catalysts had no effect on the extent of isomerization. About 8 to 9% *trans* isomers were produced when iodine value dropped 15 units. Diene conjugation varied between 1 to 2% in all cases. A selectivity of 13-14 was achieved with all catalysts except the catalyst dried at 110 C (No. 2) and the one that was heat activated at 650 C (No. 11) which had diminished slectivity.

The freeze-dried catalyst of this study is nearly as active as the supported catalysts (5,6) whose relative catalyst activities were calculated as 3.50 and 4.07. However, the present catalyst has the added advantage of being cheaper to produce, since expensive silica support was eliminated. This catalyst has potential commercial value, since it is more active than copper-chromite and yet it is expected to be no more expensive to produce.

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