Pilot-Plant Selective Hydrogenation of Soybean Oil: Activation and Evaluation of Copper-Containing Catalysts[1]

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Abstract

In pilot-plant tests, the linolenate content of soybean oil was reduced to less than 1% without increasing the saturates, by hydrogenation to an IV of about 115 with an active copper-chromite catalyst. The linolenate-linoleate selectivity ratio (K_{Le}/K_{Lo}) was from 9 to 12. Several commercial copper-chromite catalysts were used in hydrogenation tests. The activities of four of five commercial catalysts tested were improved to various degrees by heating in air at 350 C (one was inactive both before and after heating). Examination by differential thermal analysis (DTA) of each catalyst, just as received and then after being heated at 350 C, demonstrated that heating greatly diminished or removed peak areas from the DTA curve. Studies made with one commerical copper-chromium-barium catalyst showed that heating the catalyst was also necessary to gain maximum linolenate-linoleate selectivity in hydrogenating soybean oil.

Introduction

Many scientists (9,11–14,16,17) have described the hydrogenation of soybean oil using copper-chromite catalysts of the Adkins type (1,2,7,8,18). Some of these investigators were able to obtain linolenate-linoleate selectivity ratios (K_{Le}/K_{Lo}) of from 6 to 13 and linolenate was hydrogenated to less than 1% without the formation of saturates.

We found that a fresh batch of one commercial copper-chromium-barium hydrogenolysis catalyst failed to catalyze hydrogenation of soybean oil. A change of operating conditions within practical limits of pressure and temperature did not improve results. We then discovered that this catalyst could be activated by heating it in a muffle furnace at 350 C before hydrogenation.

No report was found in the literature about a method for predicting the activity of a metallic catalyst suitable for the hydrogenation of soybean oil. Differential thermal analysis (DTA) has been used to study structural and compositional changes of catalyst supports, such as alumina, and of ceramics and insulating materials. DTA techniques applied to copper-chromite catalysts prepared in our laboratory revealed changes in the catalyst during heating at 350 C (indicated in a family of thermograms representing catalysts heated for various lengths of time). Usually these changes were necessary for a copper-chromite catalyst to reach its greatest activity. Interpretation of thermogram profiles will help a processor predict the effectiveness of a copper-chromite catalyst.

Experimental Procedures

Catalysts

Nine copper-chromium catalysts (containing 16% to 40% Cu) from three commercial suppliers were tested. These catalysts are designated by capital letters A through I (Table I).

Tests with a commercially reduced nickel catalyst (25% Ni in hardened oil) like those conventionally used to hydrogenate soybean oil provided comparative data.

Soybean Oil

Refined and bleached soybean oils (commercial) were used for all tests. Their linolenate content ranged from 6.8% to 8.0% and IV, from 126–135.

Analytical Methods

Isolated *trans* fatty acid content was determined with a Perkin-Elmer Model 337 infrared spectrophotometer according to AOCS Tentative Method Cd 14–61 (3). Diene conjugation and per cent linoleate

TABLE I

Comparison of Some Copper-Chromium Catalysts by DTA and by Hydrogenation of Soybean Oil

Catalyst, as prepared					Catalyst, heat activated (HA)				
Catalyst composition	Catalyst	DTA evaluation[a]	Hydrogenation time, min	Le, % converted	Catalyst	DTA evaluation[a]	Hydrogenation time, min	Le, % converted	Corresponding figure
Cu-Cr	A	Slightly active	370	68	A (HA)	Typical, active	65	77	2
Cu-Cr-Ba	B	Inactive	480	0	B (HA)	Typical, active	100	72	1
Cu-Cr-Mn	C	Moderately active	35	82	C (HA)	Typical, active	25	87	2
Cu-Cr-Cd	D	Questionable[b]	270	0	D (HA)	Questionable[b]	330	0	2
Cu-Cr	E	Questionable[b]	645	72	E (HA)	Typical, active	130	72	2
Cu-Cr-Ba	F	Slightly active	30	85	F (HA)	Not typical (too flat)	36	72	3
Cu-Cr-Ba	35–1	Inactive	......	0	35–7	Questionable[b]	10	65	5
Cu-Cr-Ba (HT1)	G	Inactive	130	66	....	....			4
Cu-Cr-Ba (HT2)	H	Questionable[b]	95	64	....	....			4
Cu-Cr-Ba (HT3)	I	Slightly active[b]	15	75	....	....			4

[a] Differential thermal analysis evaluations were made before obtaining hydrogenation data.
[b] A profile that does not exhibit the characteristic contour of active or nonactive Cu-Cr or Cu-Cr-Ba catalysts after DTA.

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and linolenate were measured by AOCS Official Method Cd 7–58 (3) following the procedures for conjugated and nonconjugated polyunsaturated acids. Pure methyl linolenate prepared at the Northern Laboratory by liquid-liquid extraction was the reference standard. Methyl esters for gas liquid chromatography (GLC) were made by saponifying the triglycerides and then refluxing them with alcoholic BF_3 according to Metcalfe et al. (15). Fatty acid composition of triglyceride samples was determined by GLC of their methyl esters with an F&M Model 720 gas chromatograph. This instrument was equipped with a 9 ft × ¼ in. stainless steel column, packed with 20% diethylene glycol succinate (Hi Eff 1BP) on 80–100 mesh Gas-Chrom P (Applied Science Laboratories, Inc., State College, Pa.), and with a conductivity detector bridge current of 150 ma. A 3 μl sample was inserted at an injection temperature of 300 C into the column at 210 C. The helium carrier gas rate was 75 cc/min, and the detector temperature was 320 C. Fatty acid composition determined by GLC was used to calculate the IV. Selectivity ratios (K_{Le}/K_{Lo}) were calculated with a digital computer (6) from the linolenate values (by alkali isomerization) and the linoleate values (linoleate by GLC plus conjugated dienes by UV).

Hydrogenation of the Soybean Oil

Small scale hydrogenations were carried out in a stainless steel, 1½ gal capacity (8 in. diameter) Wurster-Sanger convertor equipped with a 4 in. diameter gas dispersion agitator (5). Larger scale runs were made in a 15 gal hydrogenator. Soybean oil was charged to the convertor with 1% of copper-chromite catalyst. The vessel was purged with nitrogen and evacuated while agitating at about 1,400 rpm. While maintaining 26 in. vacuum, the oil was heated to 170 C. No hydrogenation resulted when the heat-up was conducted under hydrogen pressure instead of a vacuum.

Hydrogenation was conducted at 170 C, 30 psig. The progress of the hydrogenation was followed by sampling periodically and determining the refractive indices of filtered oil samples. When the desired refractive index was reached, the convertor was evacuated and the oil cooled to 80 C under vacuum. After the batch was filtered (with filter aid), the product and intermediate samples were analyzed. Hydrogenation conditions when nickel was the catalyst were changed to a catalyst concentration of 0.2% (0.05% Ni), a temperature of 150 C and a pressure of 5 psig.

Heat Activation of Copper-Chromium Catalysts

To prepare a heat-activated (HA) catalyst for the hydrogenation of soybean oil, 22 g of the catalyst was placed in an open evaporating dish in a muffle furnace at 350 C. Length of heating the catalyst varied between 2 min and 14 hr but was usually 6 hr. The catalyst was then withdrawn from the furnace and allowed to cool to room temperature in a desiccator.

DTA of the Prepared Catalyst

DTA was carried out on a Du Pont Model 900 Thermal Analyzer with a 4 mm standard cell, silicon carbide as the reference material and a nitrogen atmosphere. For general runs the instrument was programmed from 0 to 500 C at 15 C/min with a ΔT setting of 0.2 C/in. In some tests, the programmed sample was immediately cooled with liquid nitrogen and, without removing the sample or thermocouple from the apparatus, was reprogrammed from 0 to 500 C. Such a procedure allows a comparison between the original catalyst (the initial program) and the same catalyst after heating (the reprogram).

Absolute thermal balance between the sample and the reference was never achieved, but it was not considered essential for this study. To compensate for this imbalance and for the progressive deterioration of the thermocouple, the resultant DTA instrument curve was replotted so that the base line (no exotherm or endotherm) was horizontal when the block temperature was approximately 200–250 C. This technique allows a comparison of the thermograms of similar catalysts.

Thermal Gravimetric Analysis of the Prepared Catalyst

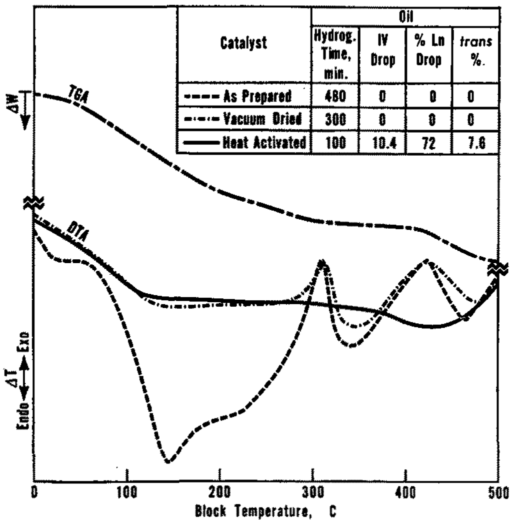
Thermal gravimetric analysis (TGA) was carried out on a Du Pont Model 950 Thermogravimetric Analyzer with about 10 mg samples. The instrument was programmed from 0 to 500 C at 10 C/min at a ΔW setting of 0.4 mg/in.

Results and Discussion

When Koritala and Dutton (12) hydrogenated soybean oil in the laboratory with commercial Cu-Cr catalysts, their K_{Le}/K_{Lo} values were from 9 to 13. They reported that an inactive commercial catalyst became active when reduced with sodium borohydride and dried.

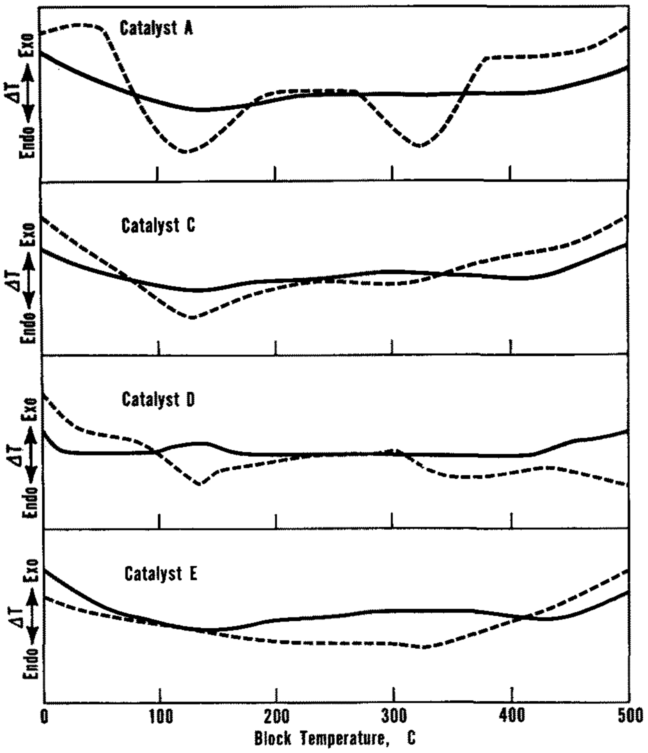
When their investigation was continued in the pilot plant with fresh batches of commercial catalysts, Catalyst B (a Cu-Cr-Ba catalyst) as received from the supplier did not catalyze the hydrogenation of soybean oil under several operational conditions tried. Drying the catalyst in a vacuum oven at 150 C minimized the initial DTA endothermic peak at 100–175 C but did not change the appearance of the exothermic peaks at higher temperatures (Fig. 1). This vacuum-dried catalyst likewise was not active.

Heat treatment of Catalyst B for 6 hr at 350 C converted it to an active form, i.e., it catalyzed the preferential rapid reaction of hydrogen with the linolenate in soybean oil. A graph of per cent converted linolenate vs. the calculated IV of the product showed that the hydrogenation of soybean oil with the activated catalyst decreased linolenate content (as



Catalyst	Oil			
	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans* %.
---- As Prepared	480	0	0	0
-·-·- Vacuum Dried	300	0	0	0
—— Heat Activated	100	10.4	72	7.6

Fig. 1. Thermal gravimetric analysis (TGA) profile and differential thermal analysis (DTA) thermogram for Catalyst B with SiC reference. Original soybean oil with IV of 126.4, 6.8% triene and no *trans* isomers.



Catalyst	A				C			
	Oil				Oil			
	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans,* %	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans,* %
---- As Prepared	370	10.4	68	7.2	35	10.4	82	7.1
Vacuum Dried	215	10.4	72	6.7	40	10.4	85	7.1
—— Heat Activated	65	10.4	77	5.8	25	10.4	87	7.1

Catalyst	D				E			
	Oil				Oil			
	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans,* %	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans,* %
---- As Prepared	270	0	0	0	~645	10.4	~72	7.8
Vacuum Dried	280	0	0	0	230	10.4	77	8.0
—— Heat Activated	330	0	0	0	130	10.4	72	~7.0

FIG. 2. DTA thermograms for Catalysts A, C, D and E with respect to SiC reference. Original soybean oil had IV of 126.4, 6.8% triene and no *trans* isomers.

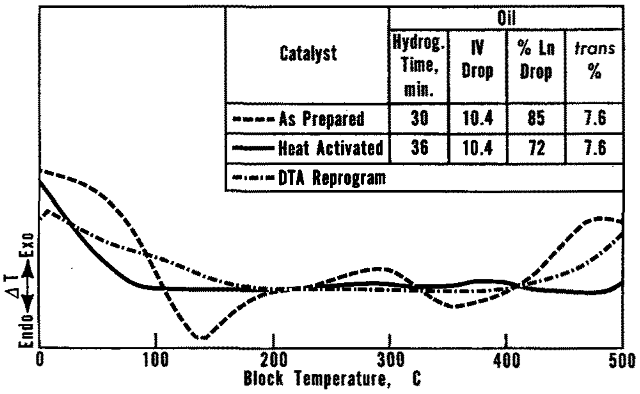
determined by alkali isomerization) by 72% of that in the original oil (Fig. 1) with an IV drop of only 10.4 units.

Catalyst B (HA) was used for five consecutive hydrogenations without the addition of makeup catalyst, however, selectivity (K_{Le}/K_{Lo}) dropped progressively from 11 to 7. Hydrogenation time to reach an IV of 120 was about doubled for the second use over the first use. Catalyst weight loss due to filtration after each reuse was not measured but was not significant.

Catalyst Examination by DTA

Characteristics of the catalysts and their corresponding hydrogenation efficiencies are summarized in Table I. Catalyst A (HA), B (HA), C (HA) and E (HA) have DTA thermograms typical of HA catalysts (Figs. 1 and 2). The absence of pronounced exotherms in the range 300 to 425 C is consistent in the thermograms of these active catalysts.

The effect of heat activation is illustrated in the DTA thermogram for Catalyst B (HA) compared to that of Catalyst B before heat activation in Figure 1.



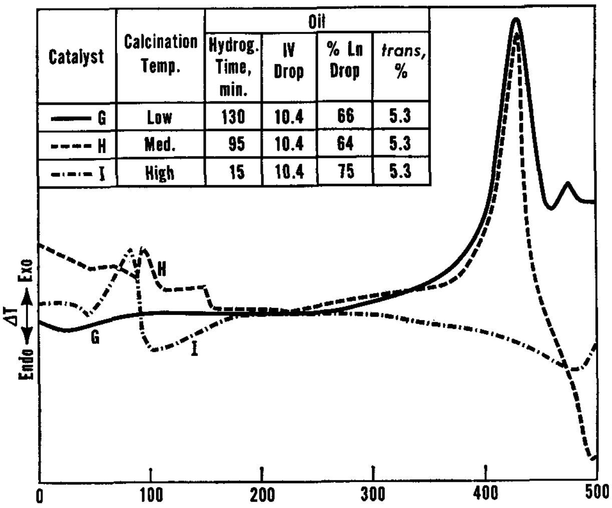
Catalyst	Oil			
	Hydrog. Time, min.	IV Drop	% Ln Drop	*trans* %
---- As Prepared	30	10.4	85	7.6
—— Heat Activated	36	10.4	72	7.6
–·–·– DTA Reprogram				

FIG. 3. DTA thermogram for Catalyst F with SiC reference. Original soybean oil had IV of 126.4, 6.8% triene and no *trans* isomers.

Subsequently DTA was conducted for each of the eight other commercial catalysts, with various heat treatments. DTA thermograms in Figures 1–3 in this report include the profile of the catalyst as it was received (-----) and the same catalyst after it was given a furnace heat activation for 6 hr at 350 C (HA) (———). For all catalysts, except Catalyst F, the HA curve coincided with its DTA reprogram curve. The DTA reprogram curve for Catalyst F (HA) is depicted in Figure 3 (—·—·—), and the reason why it did not coincide is explained later.

The nature of changes in the catalysts that occur during heat treatment, as indicated by the changes in various peaks on the DTA profile, were not determined. It is believed, however, that the first endothermic peak (100–175 C) results from partial dehydration of the catalyst. This possibility seems bolstered by the loss in weight during the TGA at about the same temperature (100–175 C) as shown in Figure 1. Catalysts G, H and I, each reportedly prepared in an unusual manner, contained an ingredient that produced an exotherm in this area; note the curves shown in Figure 4. The other two defined peaks, at about 300 and 425 C (presumed to be primarily exothermic), may result from a combination of structural changes, elimination of more tightly bound moisture and possibly conversion of the constituents to other forms. Keely (10) reports a similar thermogram for the calcination of alumina and offers a similar explanation for the changes that occurred. X-ray diffraction data for Cu-Cr and Cu-Cr-Ba catalysts before and after furnace heat activation confirm DTA observations that the catalysts underwent changes upon heating. A Cu-Cr-Ba (HA) catalyst contained larger amounts of divalent copper oxide, copper chromate and barium chromate than the same catalyst before heat treatment.

To understand the calcination step better we prepared a Cu-Cr-Ba catalyst in the laboratory. During catalyst preparation, the metals were coprecipitated as hydroxides from a solution of their nitrate salts by the addition of ammonium hydroxide according to the method of Augustine (4). Portions of the precipitate were calcined at 350 C for 2, 4, 6, 8, 10, 60, 120 min and 5½ hr. Each catalyst was then evaluated by DTA and TGA. In Figure 5 the DTA curves are shown for precipitate 35–1, which was calcined for 2 min at 350 C and for precipitate 35–7, which was calcined for 8 min (hydrogenation data in Table I). After catalyst 35–7 was acid-washed



Catalyst	Calcination Temp.	Oil			
		Hydrog. Time, min.	IV Drop	% Ln Drop	*trans*, %
—— G	Low	130	10.4	66	5.3
---- H	Med.	95	10.4	64	5.3
-·-·- I	High	15	10.4	75	5.3

FIG. 4. DTA thermogram for Catalysts G, H and I with SiC references. Original soybean oil with IV of 134, 7.3% triene and no *trans* isomers.

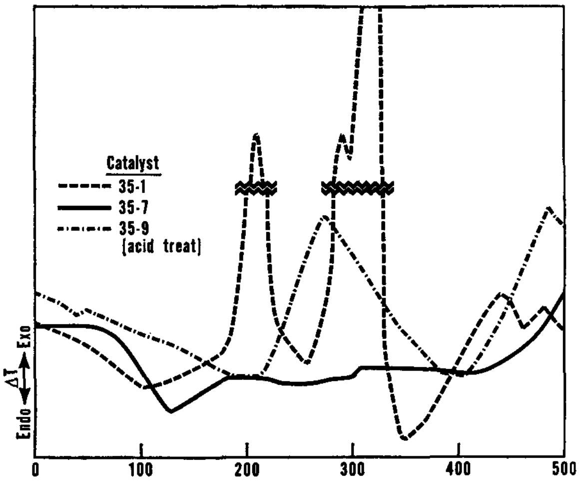


FIG. 5. Effect of calcination time upon the DTA thermogram for laboratory-prepared catalysts with SiC reference.

(followed by a water wash) its composition may have changed since exothermic peaks were present in the thermogram. Without reheating at 350 C this catalyst was as active as 35–7 (not acid washed). Upon further heat treatment at 350 C after acid washing, its thermogram was similar to a typically active catalyst, but its activity was not increased. Heating a freshly prepared catalyst at 350 C accomplishes both dehydration and oxidation, but probably oxidation is more responsible for activation of the catalyst. For example, catalyst 35–7 that was HA and then acid-washed but not reheated was quite active, although its DTA indicated that it had picked up water during the washing step.

Correlation of DTA Information With Catalyst Activity and Selectivity

Catalysts were evaluated by DTA and by actual hydrogenation of soybean oil. Catalyst A (Cu-Cr) exhibited low initial activity for hydrogenating soybean oil, and the DTA thermogram (Fig. 2) contained peaks of appreciable magnitude. After heating, Catalyst A (HA) was more active and its DTA curve was typical for an active type. Catalyst E (Cu-Cr)

TABLE II

Hydrogenation of Soybean Oil With a Copper-Chromium-Barium Catalyst Heat Treated Various Lengths of Time

Sample	Catalyst heat treatment at 350 C, min	RI^{n}_{40}	Calculated IV^{a}	Composition					*Trans*, %	K_{Le}/K_{Lo}, average	Hydrogenation time, min	Le, % converted	ΔIV
				C16^{a}	C18= 0^{a}	C18= 1^{a}	Total diene^{b}	C18= 3^{c}					
Original soybean oil, refined and bleached		1.4667	133.1	10.8	4.7	23.0	53.8	7.8	Trace	....	....	0	0
Partially hydrogenated soybean oil^{d}													
23B-1	None	1.4661	125.7	11.6	5.0	25.7	53.2	~4.5	2.4	9	20	....	7.4
-2		1.4660	120.9	11.0	4.8	30.3	51.6	2.0	6.7		60	74	12.2
-3		1.4654	116.3	10.9	4.7	35.7	48.0	0.8	10.9		120	90	16.8
25 -1	20	1.4654	124.9	10.5	4.6	27.5	55.2	2.2	5.3	13	20	72	8.2
-2		1.4650	120.5	10.7	4.6	31.5	51.8	1.4	8.0		60	82	12.6
25B-1	53	1.4660	128.5	10.5	4.5	25.9	54.5	4.4	2.7	12	20	45	4.6
-2		1.4651	122.3	11.0	4.4	28.7	53.6	2.2	6.4		60	71	10.8
-3		1.4643	115.5	10.8	4.5	36.0	48.3	0.4	11.5		85	95	17.6
26 -1	80	1.4655	124.3	10.5	4.5	28.2	54.1	2.6	4.7	12	20	67	8.8
-2		1.4650	118.5	10.5	4.6	33.3	50.6	1.0	9.2		50	87	14.6
-3		1.4644	115.9	10.2	4.5	36.5	48.4	0.4	11.8		120	95	17.2
-4		1.4640	111.2	10.5	4.7	40.6	44.1	<0.1	14.2		180	100	21.9
-5		1.4636	108.2	10.7	4.4	44.4	40.5	<0.1	17.1		240	100	24.9
-6		1.4630	105.7	10.3	4.6	47.5	37.5	<0.1	19.6		305	100	27.5
27 -1	130	1.4658	124.3	10.7	4.5	27.7	54.0	3.1	4.4	12	20	60	8.8
-2		1.4650	117.9	10.6	4.6	33.3	50.7	0.8	9.5		60	90	15.2
-3		1.4648	116.2	10.5	4.6	35.5	48.9	0.5	10.7		95	94	16.9
28 -1	180	1.4661	131.0	10.5	4.6	24.5	54.4	~5.9	Trace		20	....	3.1
-2		1.4650	119.7	10.3	4.7	32.6	51.5	0.9	9.5	14	60	88	13.4
-3		1.4647	116.9	10.5	4.6	34.7	49.7	0.5	10.7		82	94	16.2

[a] Composition determined by GLC.
[b] Composition determined by combining GLC and conjugated diene values.
[c] Composition determined by alkali isomerization (3).
[d] Hydrogenation conditions: 1% Cu-Cr-Ba catalyst, temperature 170 C, 30 psig H_2 pressure.

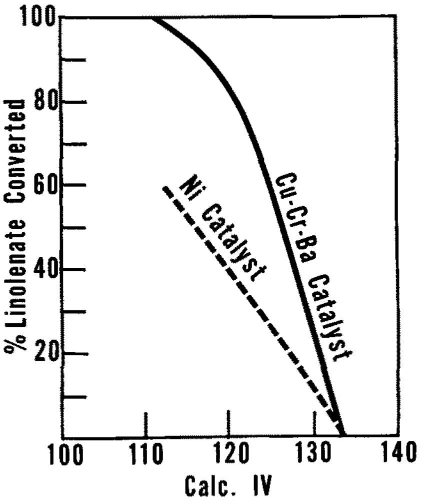


FIG. 6. Comparison of linolenate reduction by nickel and Cu-Cr-Ba catalysts during partial hydrogenation of soybean oil.

produced a similar DTA profile after heating but it was less active than Catalyst A.

Some catalysts were active as received. The DTA for Catalyst C indicated that it would be active for hydrogenating soybean oil and also that proper heat treatment might improve its activity. Catalyst C (Cu-Cr-Mn) improved only slightly by heat treatment.

Catalyst F (Cu-Cr-Ba), as received from the supplier, had a DTA thermogram with small but definite exothermic peaks. The reprogrammed DTA thermogram produced a profile of an active catalyst. This result indicated that heat treatment would be beneficial. However, during actual hydrogenation the untreated catalyst was very active. Heat treatment of 6 hr at 350 C caused the catalyst to be slightly less active. Table II illustrates the effect of heating time at 350 C for a different batch of Catalyst F upon its hydrogenation selectivity. Heating for more than 20 min at 350 C was sufficient to convert 22 g of this catalyst to a more active and selective one. The arbitrary choice of a 6 hr heat treatment was apparently too long for Catalyst F. The family of DTA thermograms for these heat-treated catalysts was similar to the reprogram curve for Catalyst F (Fig. 3).

Test hydrogenations were made on a 1 gal scale in pilot-plant type equipment to compare effectiveness of heat-activated commercial copper-chromium-barium Catalyst F with that of a commercial nickel catalyst in reducing linolenate content of soybean oil. Results of the tests are compared graphically (Fig. 6).

The much higher linolenate/linoleate selectivity of the copper catalyst (12) accounts for the complete conversion of linolenate to linoleate or oleate (or their isomers) at an iodine value of only about 111. With the nickel catalyst (selectivity about 2) conversion is only about 65% when the same iodine value is reached. The significance of these results in terms of making a soybean salad oil of high flavor stability is being studied.

Catalyst D (Cu-Cr-Cd) was inactive upon receipt and also after heat treatment (Fig. 2). It was difficult to determine from the DTA profile alone whether this catalyst might be active, since an active Cu-Cr-Cd catalyst was not available for comparison. No attempt was made to explore other hydrogenation conditions for Catalyst D. Since DTA and hydrogenation data are not always congruent, the two testing methods must complement one another, and DTA therefore cannot be used alone without further investigation.

Catalysts G, H and I (Cu-Cr-Ba) are catalysts with identical composition but said to be calcined at three different temperatures. Figure 4 compares the DTA results for these catalysts. Although none of the curves are similar to that of an active Cu-Cr-Ba catalyst from other sources, the profile for Catalyst I is devoid of exotherms above 400 C and resembles an active catalyst. Its hydrogenation activity was considerably better than the activities of Catalysts G and H.

Thus although some commercial copper-chromite catalysts, prepared for the reduction of fatty esters to alcohols, selectively hydrogenated soybean oil, other commercial catalysts were inactive as prepared and were activated only by proper heat treatment. It was not necessary to prereduce the catalyst as reported (12). A catalyst testing program based on hydrogenation data in conjunction with DTA provides useful information on hydrogenation activity of the catalyst and how to achieve maximum catalyst activity.

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