Catalytic Hydrogenation of Vegetable Oils: II. The Activity of the Prereduced Copper Chromite Catalyst

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ABSTRACT
The prereduction of copper chromite with hydrogen produces a strong deactivation of catalyst in soybean oil hydrogenation at 200 C and 6 atm. ESCA studies and kinetic data show that the decrement of the activity is correlated to the disappearance of Cu’ and Cu’’ species and to the decrement of Cu/Cr ratio on the catalyst surface. The comparison of activity between original and prereduced catalysts allows a better elucidation of the role of Cu’ in promoting the double bond conjugation and of Cu’’ in catalyzing the conjugated double bond hydrogenation.

INTRODUCTION
The copper oxide-chromium oxide system has been extensively studied in the past due to the high selectivity shown by this catalyst in the partial hydrogenation of vegetable oils (2-4). In particular, many experiments have been done to correlate catalytic properties with operational parameters such as temperature (5), hydrogen pressure (5-9), hydrogen flow (10), catalyst concentration (7,9), substrate composition (8,11) and activation procedures (12,13).

At the same time, much attention has been devoted to the characterization of the active centers present in the catalyst: different techniques, such as X-ray diffraction analysis (14-16), electron spectroscopy for chemical analysis (ESCA) measurements (14,17,18) and differential thermal analysis (DTA) determinations (19) have been used along with chemical analysis for studies of the bulk and surface properties. According to recent work, Cu’, in intimate contact with Cu2Cr2O4, seems to be the active species for the linolenate and linoleate hydrogenation (8,14) which proceeds via double bond isomerization (5,20,21).

One point subject to much speculation is the observation that the catalyst activity decreases with time (14). This behavior has been attributed to the variation of the relative concentrations of Cu’ and Cu’’ species formed during catalyst reduction (8,14).

However, much less attention has been given to the catalyst activity toward conjugated polyenes. In fact, limited kinetic data given in the paper of Koritala and Selke, who observed deuterium-hydrogen exchange and double bond isomerization during the deuteration of conjugated dienes (11), do not allow any comparison between these substrates and the nonconjugated analogs.

Also little studied were the activity and the selectivity of prereduced copper chromite catalysts which show a higher content of Cu’’ on the surface than those obtained by reduction in the presence of the substrate.

These observations prompted us to extend our previous studies on the selective hydrogenation of polyenes (22,23) to the copper oxide-chromium oxide system to elucidate the role of copper, in different oxidation states, as catalyst for the hydrogenation of nonconjugated and conjugated isomers of fatty acid molecules.

EXPERIMENTAL PROCEDURES
The catalyst normally used was a modified commercial copper chromite (GIRDLER G-89) supplied by Sud-Chemie A.G., with the following composition: 37.1% Cu, 27.4% Cr and 0.78% Mn. ESCA measurements also were carried out on an Mn-free copper chromite containing only the phases CuO and CuCr2O4 (GIRDLER G-13). The catalysts were heated at 350 C in air for 6 hr before use.

Soybean oil was a refined and bleached commercial product, with the following gas liquid chromatographic (GLC) composition: C16:0=11.5%; C18:0=3.5%; C18:1=23.2%; C18:2=54.7%; C18:3=7.1%.

Soybean oil methyl esters were prepared by transesterification with methanol catalyzed by sodium methoxide, and purified by distillation under reduced pressure.

Soybean oil conjugated methyl esters were prepared by a slightly modified analytical method (24): in a stainless steel autoclave (150-mL) 10 g soybean oil, 6 g NaOH and 100 mL CH3OH were heated at 190 C for 3 hr under nitrogen atmosphere with magnetic stirring. After cooling, the soapy past was transferred into a 2L flask and 1 L of H2O was added. The resultant solution was treated with diluted H2SO4 (1:10, v/v) in slight excess. The free fatty acids were extracted with petroleum ether and dried over Na2SO4. After solvent evaporation, the methyl esters were obtained by esterification with a BF3/CH3OH solution, and purified by distillation under reduced pressure (conjugated dienes = 32.7% by ultraviolet [UV] analysis).

Reduction of Copper Chromite with Hydrogen
A sample (0.1-1 g) of G89 or G13 catalyst was introduced into a glass reactor which had a long, air-cooled neck, and heated for 0.5 hr under vacuum at 270 C in a thermostatic device. Then hydrogen at 0.9-1 atm was carefully introduced.

A fast reduction took place as indicated by the water condensation on the cold arm of the reactor. From time to time, the condensate was purged under vacuum and, finally, hydrogen was replaced with nitrogen after cooling at room temperature. The reduced catalysts (G89R and G13R) appear as black, finely divided powders that are unstable to atmospheric oxygen. They were handled under nitrogen atmosphere (41.4% Cu; 29.5% Cr and 0.85% Mn for G89R). After solvent evaporation, the methyl esters were obtained by esterification with a BF3/CH3OH solution, and purified by distillation under reduced pressure (conjugated dienes = 32.7% by ultraviolet [UV] analysis).

Recovery of Used Copper Chromite Catalyst
A sample of G89 or G13 (1.5 g) was suspended in 500 mL of soybean oil and introduced into a 1 L stainless steel autoclave. The temperature was raised, under vacuum, to 200 C and hydrogen was introduced at 6 atm. The mixture

1 For part I, see ref. 23.
was stirred at 600 rpm for a suitable time (1.5 hr for the catalyst referred to in the text as G89U) at constant hydrogen pressure. The autoclave was then rapidly cooled to 80 C, the slurry transferred under nitrogen atmosphere into a 1.5 L flask and diluted with 500-mL of dried, deaerated petroleum ether. The solid, collected in a paper thimble, was purified in a Soxhlet apparatus by extraction with petroleum ether under nitrogen atmosphere and dried under vacuum.

Hydrogenation Reactions

A mixture of catalyst and deaerated substrate was introduced under vacuum into a preheated, stainless steel autoclave (150 mL) provided with magnetic stirring and a sampling device. Hydrogen was then introduced at suitable pressure and stirring was started. During the reaction, the pressure was kept constant by supplying hydrogen.

Reactions at atmospheric pressure were carried out in an all-glass reactor which was connected, through a water-cooled arm, to a gas burette. Detailed experimental conditions are reported in the tables and figures.

Analytical Methods

The methyl esters from soybean oil were analyzed with a Hewlett Packard 5880A gas chromatographic apparatus using a 6 ft X 1/8 in. stainless steel column packed with 10% EGSSX on 100/120 Chrom P.

C18 methyl esters, purchased from C. Erba, were used as standard.

The amount of conjugated polyenes was evaluated by a UV method (24) using a Cary 219 UV spectrophotometer.

The metal content of the bulk of the catalysts was determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer 305 instrument. The samples were dissolved by wet digestion with boiling concentrated perchloric acid.

X-ray photoelectron (XPE) spectra were done using a Vacuum-Generator ESCA 3 spectrometer with Al K source (hv = 1486.6 eV). Binding energies were referred to the Au f7/2 (b.e. = 84.0 eV) and C ls (b.e. = 285.0 eV) was used as internal standard for calibration and correction of charging effects (25).

RESULTS AND DISCUSSION

Catalytic systems having different surface amounts of Cu° and Cu' can be obtained by sampling the copper chromite catalyst (Girdler--G89 or G13) during the hydrogenation of soybean oil at 200 C and 6 atm of H2.

ESCA measurements obtained by us (26-28) on such samples are consistent with the data previously reported (14-18).

Thus, a fast reduction of Cu" during the use of G13 and G89 catalysts is shown by the shift of Cu2P binding energies to low values (Table I) and by the gradual disappearance of the satellite structure (Fig. 1). In addition, the presence of separated peaks, ca. 2.3 eV, in Auger LMM (25) spectra of used G13 and G89 indicates the formation of Cu° and Cu' species.

In fact, such a separation has been observed in the case of pure samples of Cu metal and Cu2O (27,28). The Cu° species increases during the hydrogenation reaction, as shown by the relative peak intensities (Fig. 2), although a small amount of Cu' is still present even after a long reaction time (120'). This agrees with studies of other authors who have found ca. 5% of Cu' in catalysts used for similar long times (8,14).

In the case of Mn-free catalyst, G13, we also derived information on the surface dispersion of copper. In fact,