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Catalytic Hydrogenation of Vegetable Oils:
III. A Comparison of Reactivity and Selectivity between Cyclic Polyenes and Polyunsaturated Fatty Acids with Copper Chromite as Catalyst

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The catalytic activity of untreated and pre-reduced copper chromite in the hydrogenation of cyclic polyenes has been investigated. A comparison is made with the hydrogenation of polyunsaturated fatty acids of soybean oil. The role of the different oxidation states of the copper and the influence of the geometry of the substrate on the hydrogenation rate are discussed.

Introduction

During the last few years the copper oxide–copper chromite [1] ($CuO–CuCr_2O_4$) system has drawn increasing attention for the partial hydrogenation of polyunsaturated fatty acids (linoleic and linolenic) present in vegetable oils. In fact, in spite of lower activity with respect to other systems like Ni Raney, such interest is due to the high selectivity polyene–monoene [2–4] obtainable with this catalyst in a wide range of experimental conditions [5–12] and therefore many investigations have been made in order to elucidate the nature and the role of active centers present on the surface of this catalytic system [13–17].

Although the fast reduction of bivalent copper to Cu(I) and Cu(0) species during the hydrogenation experiments has long been recognized, recent reports only deal with the nature and activity of the surface catalytic centers [13–16].

We have recently differentiated more clearly the contribution of Cu(0) and Cu(I) to the overall activity in the hydrogenation of vegetable oils. In particular we have compared (by E.S.C.A. measurements) the surface composition and the catalytic behaviour of a copper chromite before and after pre-reduction treatment.

Auger spectra indicate that, on the surface of the pre-reduced catalyst, the copper is almost exclusively present as Cu(0) whereas, on the surface of the untreated catalyst recovered after various reaction times during the hydrogenation of soybean oil, the Cu(I) species is still present in appreciable amount (≃5%) even after a long time [13, 17, 18]. This different surface composition causes a dramatic effect on the hydrogenation rate and selectivity: in the hydrogenation of soybean oil carried out at 200 °C and 6 atm H_2 the untreated catalyst is active, whereas the pre-reduced one is almost inactive. The latter on the other hand is very active in the hydrogenation of preconjugated soybean oil methyl esters even under milder conditions (140 °C, 1 atm H_2) [18].

This trend suggested that, in the hydrogenation of polyunsaturated fatty acids, the Cu(I) is the active species devoted to the conjugation of isolated double bonds while Cu(0) is only able to hydrogenate the conjugated polyenes [17, 18].

In order to evaluate the influence of the nature and geometry of the substrate on the catalytic activity and selectivity of these copper chromite systems, we have extended our studies to the hydrogenation of the cyclic polyenes 1,3,5-cycloheptatriene, 1,3-cyclooctadiene and 1,5-cyclooctadiene. Our interest for these substrates is due to the fact that the corresponding monoenes are largely employed in the chemical industry as useful intermediates in the synthesis of bicarboxylic aliphatic acids, ketones, cyclic alcohols, lactones, etc.

Experimental Section

Cycloolefins (supplied by Fluka) were distilled, purified by filtration on alumina and stored under nitrogen atmosphere at 0 °C. Reagent-grade Nujol, deaerated and stored under nitrogen, was used as solvent.

The untreated catalyst was a commercial copper chromite (Girdler G 89) supplied by Sud Chemie

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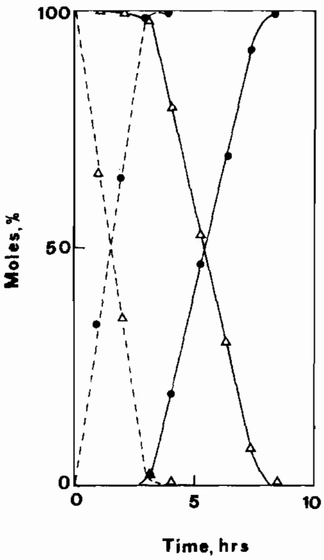


Fig. 1. Molar percentage of the reaction products in the hydrogenation of 1,3-cyclooctadiene at 140 °C and 1 atm, catalyzed by G 89 (———) or G 89R (------); key: △ = 1,3-cyclooctadiene; ● = cyclooctene.

A.G., having the following composition: Cu, 37.1; Cr, 27.4; Mn, 0.78%.

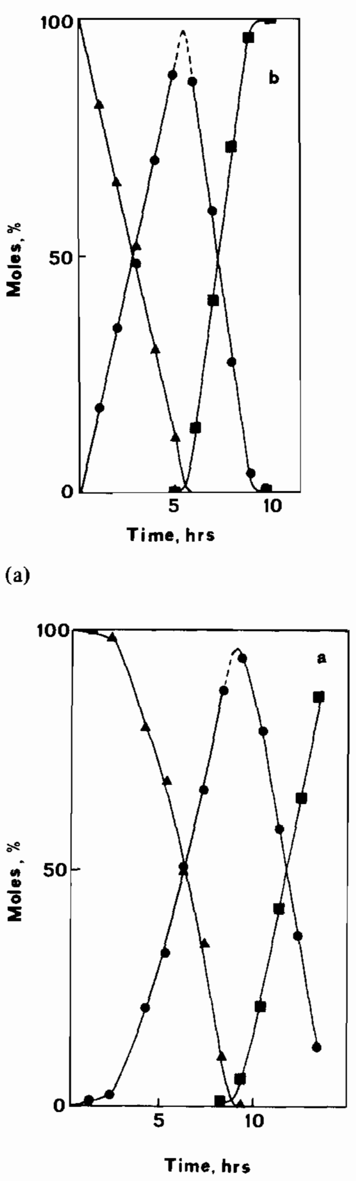
The catalyst was heated at 350 °C in air for 6 h before use. When needed, the copper chromite was pre-reduced with hydrogen according to the previously reported procedure [18]. The reduced catalyst (indicated as G 89R) a black, finely divided powder unstable to atmospheric oxygen, was handled under nitrogen atmosphere (Cu, 41.4; Cr, 29.5; Mn, 0.85%).

Reactions at atmospheric pressure were carried out in all-glass reactor connected, through a water cooled arm, to a gas burette. When a hydrogen pressure of 6 atm was used, the reactor was a stainless steel AISI 316 autoclave (150 ml) provided with a sampling device. In all experiments a nujol solution of substrate 0.85 *M* was used, and the catalyst concentration was 0.3% w/v.

The composition of reaction mixtures was analyzed by G.L.C. with a 50 m × 0.2 mm Carbowax 20 *M* capillary column using a Hewlett-Packard 5880 A instrument.

Results and Discussion

When a nujol solution of 1,3-cyclooctadiene is hydrogenated at 140 °C and 1 atm of H_2 in the presence of the untreated copper chromite (G 89), an induction time of *ca.* 2 h is observed, followed by selective reduction of the diene to cyclooctene, with a cyclooctane content less than 0.5% at a 1,3-cyclooctadiene conversion of 99% (Fig. 1).



(a)

(b)

Fig. 2. Molar percentage of the reaction products in the hydrogenation of 1,3,5-cycloheptatriene at 140 and 1 atm, catalyzed by G 89 (a) or G 89R (b); key: ▲ = 1,3,5-cycloheptatriene; ● = 1,3-cycloheptadiene; ■ = cycloheptene.

During the induction time, according to the E.S.C.A. and kinetic data previously reported [13, 15, 17, 18], Cu(II) on the surface of the catalyst is reduced to a mixture of Cu(I) and Cu(0), the latter being the active species in the hydrogenation of the conjugated diene [18].

Using the pre-reduced catalyst (G 89R), in which according to the reported E.S.C.A. data surface copper is present exclusively as Cu(0) [17, 18], the reaction takes place without any induction time (Fig.

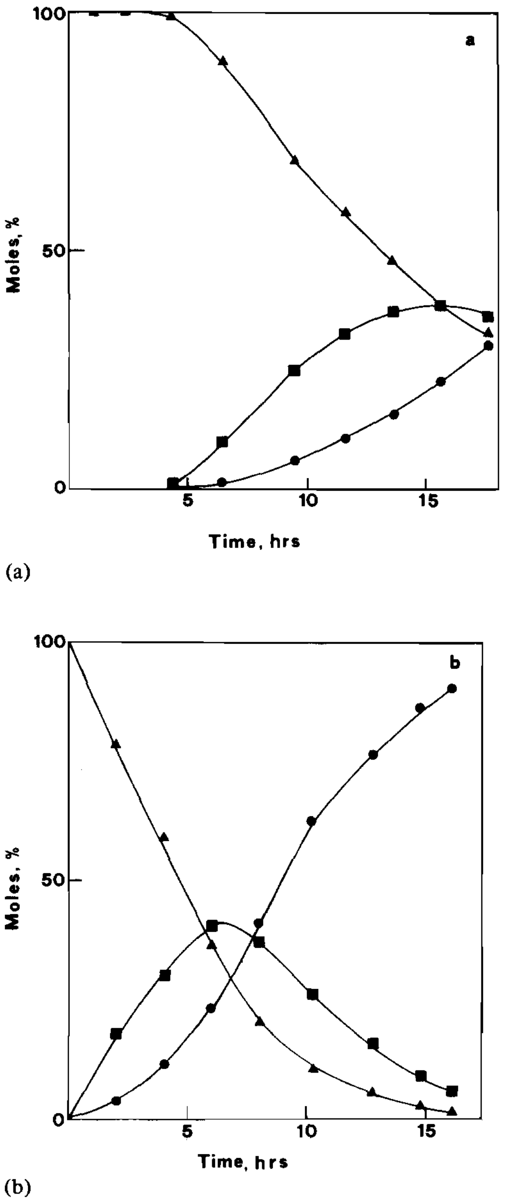


Fig. 3. Molar percentage of the reaction products in the hydrogenation of 1,5-cyclooctadiene at 140 °C and 1 atm, catalyzed by G 89 (a) or G 89R (b); key: ▲ = 1,5-cyclooctadiene; ■ = 1,4-cyclooctadiene; ● = cyclooctene.

1); the higher rate found in this case agrees with the greater surface amount of Cu(0). Besides, the absence of the induction time is observed in the hydrogenation of 1,3,5-cycloheptatriene catalyzed by the pre-reduced G 89R (Fig. 2b) whereas, as expected, a 2 h induction time is observed using G 89 catalyst (Fig. 2a). In such a case the reaction occurs in two steps: initially 1,3,5-cycloheptatriene is selectively reduced to 1,3-cycloheptadiene, and this starts to hydrogenate when the triene is almost completely reduced (cycloheptatriene conversion of 97%).

Using 1,5-cyclooctadiene as substrate and untreated G 89 as catalyst at 140 °C and under atmospheric pressure of hydrogen, the hydrogenation reaction takes place at an appreciable rate after an induction time of *ca.* 3 h. This reaction, as shown in Fig. 3a, proceeds by a step mechanism involving isomerization of 1,5-cyclooctadiene to 1,4-cyclooctadiene, which in turn gives 1,3-cyclooctadiene. This conjugated isomer is not accumulated but is selectively and rapidly hydrogenated to cyclooctene.

It should be pointed out that under the same conditions hydrogenation of non-conjugated soybean oil fatty acids does not occur at an appreciable rate even after several hours [18]. The rate of hydrogenation of soybean oil becomes high at 200 °C and 6 atm of H_2 [13, 18].

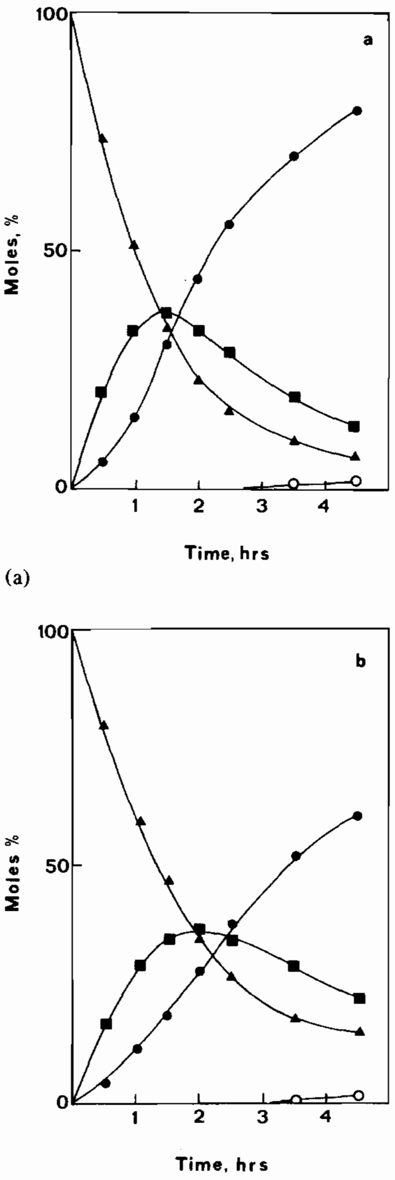
The difference in reactivity between 1,5-cyclooctadiene and the non conjugated polyenes in soybean oil is even greater when we use pre-reduced, Cu(I) free, G 89R catalyst (Fig. 3b). In fact, 1,5-cyclooctadiene at 140 °C and 1 atm H_2 is isomerized and then hydrogenated, without any induction time, with a rate greater than that observed with G 89, whereas soybean oil (with G 89R) is not hydrogenated under even more severe conditions [18] (200 °C, 6 atm H_2).

These results prove that unlike soybean oil non-conjugated polyenes the isomerization reaction of 1,5-cyclooctadiene occurs also in the absence of Cu(I) species on the catalyst surface.

In order to further elucidate the catalytic role of Cu(I) we have carried out the hydrogenation of 1,5-cyclooctadiene, both with G 89 and G 89R, under the same conditions used for the hydrogenation of soybean oil (200 °C and 6 atm H_2). As pointed out before, under such conditions the Cu(II) on the surface of the untreated G 89 is reduced in a few minutes to a mixture of Cu(I) and Cu(0) [13, 15, 17, 18]. As shown in Figs. 4a and 4b, no induction time is observed with both catalysts and the isomerization reaction is slightly faster in the case of G 89 (containing Cu(I) and Cu(0) mixture [17, 18]) than with G 89R (containing only Cu(0) [17, 18]).

This trend also suggests that in the case of these more reactive cyclic polyenes, Cu(I) plays the already-observed role in the isomerization of non-conjugated double bonds [18].

However these cyclic substrates are able to isomerize even in the presence of catalysts containing only Cu(0) on the surface: in this respect lies the intrinsic greater reactivity of 1,5-cyclooctadiene, compared to non-conjugated polyunsaturated fatty acids, characterized by long open chains. This unexpected behaviour can possibly be correlated to the constricted conformation of the double bond in



(a)

(b)

Fig. 4. Molar percentage of the reaction products in the hydrogenation of 1,5-cyclooctadiene at 200 °C and 6 atm, catalyzed by G 89 (a) or G 89R (b); key: ▲ = 1,5-cyclooctadiene; ■ = 1,4-cyclooctadiene; ● = cyclooctene; ○ = cyclooctane.

1,5-cyclooctadiene, which might favour a chelate-coordination toward the Cu(0).

Therefore, we suppose that the failure of Cu(0) to catalyze the isomerization reactions of long open chain 1,4-dienes [18] can be due to a lower chelating power of these flexible, sterically-hindered molecules on the Cu(0), compared to Cu(I), rather than to a complete inability of Cu(0) to promote isomerization reactions.

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