A New Catalyst for the Selective Hydrogenation of Sunflower Seed Oil

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A new Ni catalyst supported on sepiolite has been prepared by the precipitation/deposition method. Its activity and selectivity was tested in the hydrogenation reaction of sunflower seed oil. The variables studied were active phase concentration, reaction temperature and stirring speed. For contrasting purposes, a commercial catalyst designed for the same objective by Süd Chemie A.G. (Munich, Germany), G-53, was also tested under the same set of conditions. Selectivity to oleic acid with the new catalyst was appreciably better. The activation energies obtained with both catalyst were of the same order and within the range of those found in the literature for conventional nickel catalysts.

KEY WORDS: Activation energy, catalyst activity, gas-liquid chromatography, hydrogenation of oil, kinetic reaction, methyl esters, Ni/sepiolite catalyst, precipitation method, reaction temperature, selectivity.

The discovery by Normann (1) of the fat hydrogenation process gave rise to the development of a powerful industry, which manufactures a series of fatty products for many different purposes. The aim of the hydrogenation process is the total or partial saturation of the double bonds of unsaturated fats. The product obtained depends on the nature of the starting oil, on the type and concentration of the catalyst used and on the concentration of hydrogen, as well as on the experimental conditions under which the reaction takes place. Various authors (2–4) affirm that the rate constant and selectivity ratio of the reaction depends on parameters such as hydrogen pressure, temperature and stirring speed. Hard hydrogenated fats are necessary in the manufacture of high-quality vegetable margarine and shortenings for edible purposes, and their production is achieved by selective hydrogenation under the appropriate set of conditions.

With this aim, different metal-supported catalysts have been used in the hydrogenation of edible oils, among them Cu, complexes of Cr and Pd (5–7) and mainly Ni (8–11) because of its low cost and inert nature with respect to oil. The commercial supports currently used are silica, carbon and kieselguhr.

The catalyst introduced in this work uses sepiolite as a support and the active phase (Ni) is incorporated by the precipitation/deposition method described by Van Dillen *et al.* (12).

The object was to seek a cheaper and more efficient alternative to the conventional industrial catalysts by studying the metal/support interaction, looking for its incidence in the activity and selectivity results and in comparison with those obtained with an industrial catalyst under the same conditions.

EXPERIMENTAL PROCEDURES

The support used was sepiolite, a magnesium silicate with a mineralogical formula of $Si_{12}Mg_8O_{32} \cdot nH_2O$ and a fibrous morphology, which provides for a surface area of 136 m^2/g after thermal stabilization and a pore volume of 0.358 cm^3/g, essentially in interparticular mesopores. It was supplied by TOLSA and comes from Toledo (Spain). The main reasons for choosing the present support have been its suitable textural characteristics and its abundance and low cost in Spain.

The supported nickel catalyst was prepared from a 0.13 M solution of $Ni(NO_3)_2 \cdot 6H_2O$ by homogeneous precipitation of $Ni(OH)_2$ through urea, which gives a constant pH around 6 and a concentration of $[OH^-]$ sufficient to force the active phase to make use of the sepiolite surface silanols giving rise to antigorite. The final catalyst was designated SYP.

In the Süd-Chemie A.G. (Munich, Germany) commercial catalog, the catalyst G-53 is suggested for obtaining the unsaturated fatty acid mix required in edible oils, from the selective hydrogenation of vegetable oils, and for this reason it was chosen for comparison with our present catalyst. The protection fat of catalyst G-53 was dissolved by elution of the fatty components with diethylether. The solution was filtered through a dry filter paper.

The measurement of the catalysts' surface area (S_{BET}) was accomplished by the N_2 adsorption-desorption isotherm at 77°K in a Micromeritics Digisorb 2600 (Norcross, GA). Surface areas were calculated from the first part of the isotherms ($P/P_0 < 0,3$) by using 0.162 nm^2 as the cross-sectional area of the adsorbed nitrogen molecule.

Nickel content was determined by atomic absorption in a Perkin-Elmer apparatus (Norwalk, CT) after acid digestion of the samples in a Politetrafluoroethylene (Teflon) reactor (PTFR) autoclave by following Langmuyr and Paus method (13).

The particle size of the metallic phase was determined by transmission electron microscopy (TEM) on a Philips 300 instrument (Cincinnati, OH). The metallic surface area (S_{Ni}) was calculated from the metallic particle size (d_{MET}).

The hydrogenations were carried out in a 500-mL Pyrex glass batch reactor with 100 g oil per experiment. The thoroughly refined commercial sunflower seed oil (acidity < 0.2% oleic acid) used in the reaction had the following acid composition: $C_{16:0}$, 7%; $C_{18:0}$, 5%; $C_{18:1}$, 29%; $C_{18:2}$, 59%. Its iodine value calculated from gas-liquid chromatography (GLC) was 126. Various active phase/oil ratios were evaluated during this study, and the selected one for each standard experiment was 0.05%. The flow of H_2 bubbling through the oil was 200 cc/min. The temperature of the catalytic bed was measured with a thermocouple placed in the bottom of the reactor, enclosed in a glass sleeve for protection. Unless otherwise stated, stirring speed of 1400 r.p.m. was used throughout the reaction.

The composition of the products was analyzed by GLC in a packed column with 20% DEGS over Chromosorb B (Supelco, Bellefonte, PA) and isothermally heated to 170°C.

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The difficulty of working with acids, due to their polarity, was overcome by periodically taking samples from the reactive oil and preparing the corresponding methyl esters from them by the Metcalfe and Wang method (14) with tetramethylammonium hydroxide (TMAH) as a catalyst.

Catalytic activity was determined from the rate constants obtained from the conversion data of linoleic acid ($C_{18:2}$) to oleic acid ($C_{18:1}$). Selectivity to oleic acid, defined as the ratio between the obtained oleic acid and the reacted linoleic acid, was studied throughout the reaction.

RESULTS

The most significant characteristics of the catalysts used in this work are shown in Table 1.

The hydrogenations were carried out at temperatures between 180 and 200°C, stirring speeds were in the range of 600 to 1800 r.p.m., and active phase concentrations were between 0.025 and 0.100% (on a Ni basis). The progress of the reaction was followed by chromatographic analysis of the hydrogenated products with time.

Catalyst activity. As hydrogenation is a triphasic reaction that takes place on the surface of the solid catalyst, the diffusion phenomena become particularly important. Therefore, the degree of agitation of the reacting mixture affects the activity and selectivity ratio to a great extent. The changes in reaction rate with different stirring speed are shown in Table 2. Since no influence is detected above 1200 r.p.m., 1400 r.p.m. was chosen for all further experiments.

More important is the effect of temperature on the activity and selectivity of the catalysts. The composition/time graphs for linoleic, oleic and stearic acids at 180°C on both catalysts are shown in Figure 1. After an initial induction period, there was linearity up to around 90% conversion, so that the kinetics of hydrogenation can be considered to be zero order with respect to the conversion of linoleic acid.
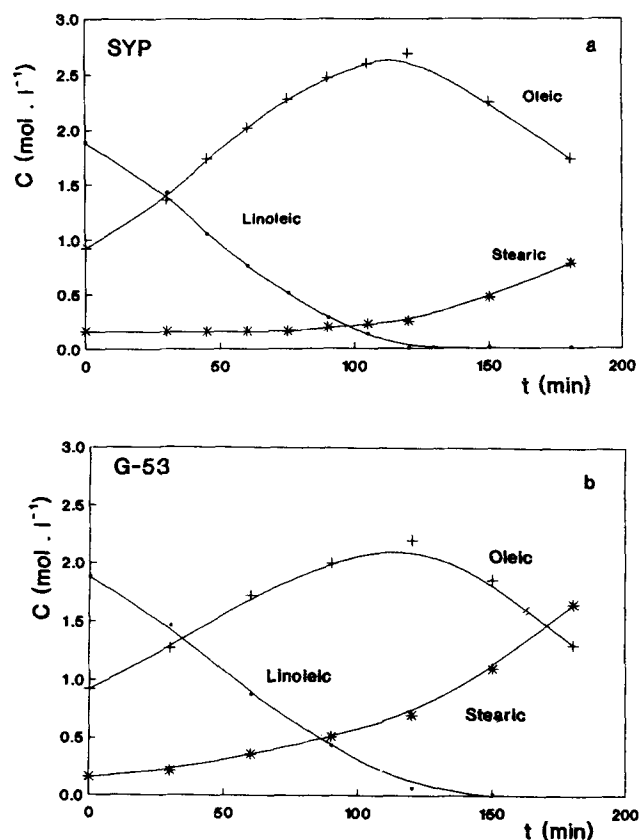

FIG. 1. (a) Hydrogenation kinetics of sunflower seed oil at 180°C on SYP catalyst. (b) Hydrogenation kinetics of sunflower seed oil at 180°C on G-53 catalyst.

The values of the kinetic constants and catalytic activity obtained with each catalyst, with respect to the disappearance of linoleic acid at the three working temperatures, 180, 190 and 200°C, are presented in Table 3.

The values of the rate constants at different temperatures were used to calculate the apparent activation energy according to the Arrhenius equation:

$$k = A \cdot e^{-Ea/RT} \qquad [1]$$

By presenting ln K *versus* 1/T in Figure 2, two straight lines are obtained from whose slopes are calculated the values of the activation energy. They are 10.4 Kcal/mol

TABLE 1

The Main Characteristics of the Investigated Catalysts

	SYP	G-53
S_{BET} (m²/g)	144	109
Ni (%)	12	48
d_{MET} (Å)	95	99
S_{Ni} (m²/g$_{Ni}$)	60	57

TABLE 2

Reaction Rates as a Function of Stirring Speed

r.p.m.	r_L (× 10⁻²) (mol·L⁻¹ · min⁻¹)
600	1.02
800	1.33
1200	1.90
1400	1.92
1800	1.95

TABLE 3

Catalysts' Kinetic Constants and Activities at Different Temperatures

Catalyst	T (°C)	k (× 10⁻²)[a]	Activity (× 10⁻²)[b]
SYP	180	2.06	41.2
	190	2.71	54.2
	200	3.23	64.6
G-53	180	1.92	38.4
	190	2.57	51.4
	200	3.20	64.0

[a] Speed constant in mol·L⁻¹·min⁻¹.
[b] Activity in mol·L⁻¹·min⁻¹·g⁻¹.
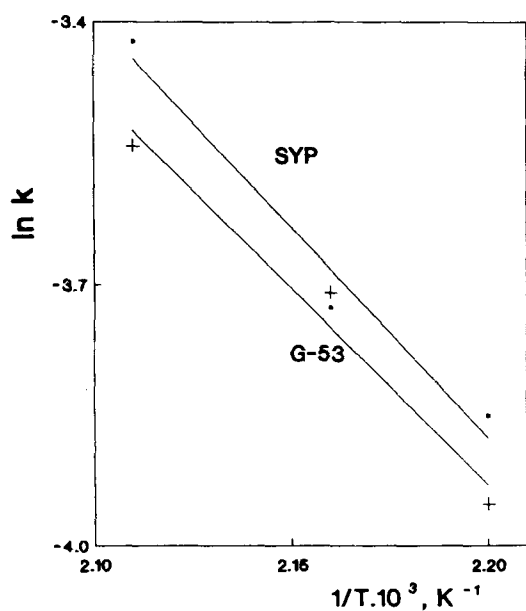
FIG. 2. Arrhenius equation for SYP (●) and G-53 (+) catalysts.

FIG. 3. (a) Influence of the active phase concentration on selectivity. (b) Influence of the temperature on selectivity.

for the SYP catalyst and 11.1 Kcal/mol for the commercial G-53; the values obtained were within the range of those given in the literature (15) for nickel, 8–12 Kcal/mol.

Catalyst selectivity. Likewise, a study was made of the influence of Ni concentration and working temperature on the selectivity to oleic acid. It was found that the higher the Ni active phase concentration, the lower the selectivity to oleic acid. According to Figure 3a the selectivity to oleic acid is 100, 98 and 82%, respectively, in accordance with the increasing percentage of Ni used, *i.e.* 0.025, 0.050 and 0.100%. Figure 3b shows that the variation of selectivity with temperature at 60% conversion is 100, 96, 92% at 180, 190 and 200°C, respectively. Figure 4 shows the variation of selectivity with conversion on both catalysts; at total conversion, a selectivity ratio of 94% on Ni-sepiolite is achieved, whereas only 68% is attained on the commercial G-53 catalyst.

DISCUSSION

The activity achieved with the sepiolite-supported catalyst introduced here, with a load of 12% nickel, is of the same order as that achieved with the commercial catalyst, which has an active phase content up to four times higher. Because the hydrogenation properties of catalysts are mainly defined by their porous structure and the commercial catalyst used kieselguhr (a macroporous solid) as a support, a major part of the nickel active phase must be occluded inside the macropores and is not accessible to the large triglycerides molecules and, therefore, not of any use in the reaction. In contrast, all the active phase was precipitated on the sepiolite external surface, where no steric hindrance with the reactant can occur. Specific activity was much improved and, therefore, the economics of the process. Other economical advantages arise from the catalyst preparation step because sepiolite can be used without any additional activation process.

Although the catalyst activity was of the same order in both catalysts, this was not the case with respect to
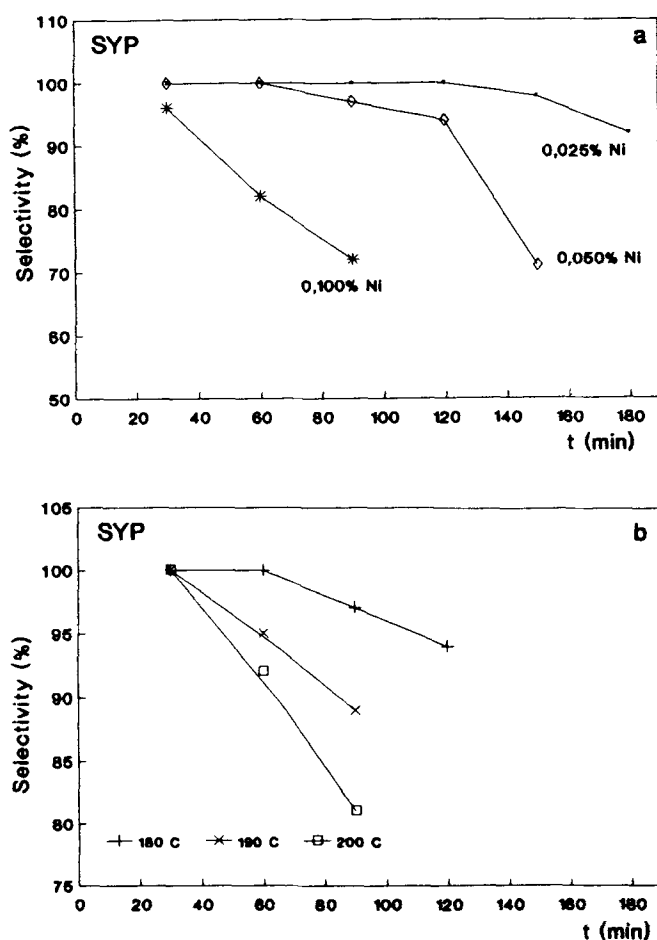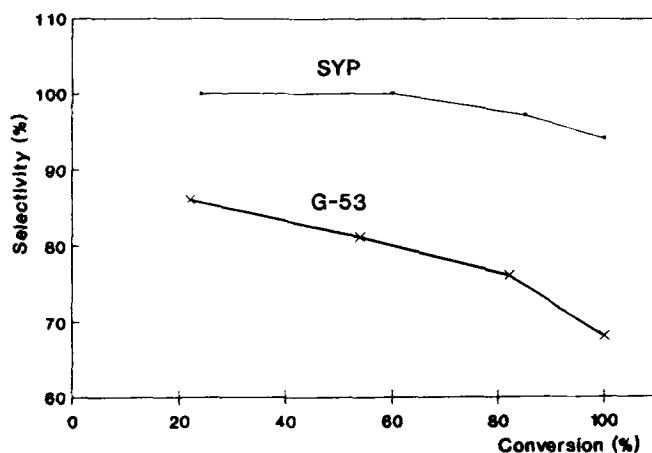

FIG. 4. Selectivity *vs.* conversion for SYP (●) and G-53 (+) catalysts.

selectivity to oleic acid, which was higher on the sepiolite-supported catalyst than on the industrial catalyst.

From all this it can be deduced that sepiolite presents a profitable alternative as a support for nickel catalysts in relation to conventional supports, when similar methods of active phase incorporation are used.

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