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Influence of Ni–Cu alloying on Sepiolite-supported nickel catalysts in the liquid-phase selective hydrogenation of fatty acid ethyl esters

F.M. Bautista, J.M. Campelo, A. Garcia, R. Guardoño, D. Luna ^{*}, J.M. Marinas

Department of Organic Chemistry, University of Córdoba, San Alberto Magno Av., E-14004 Córdoba, Spain

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Abstract

The role of Cu in Sepiolite-supported bimetallic Ni–Cu catalysts has been evaluated through the results obtained in a kinetic study on the influence of temperature in the consecutive hydrogenation of ethyl linolate to ethyl oleate and ethyl stearate, respectively. Liquid-phase hydrogenation reactions (individual and consecutive) were carried out under hydrogen pressure of 0.41 MPa in a temperature range between 305 and 337 K. Thus, the relative reactivities of linoleic and oleic ethyl esters, $R_{L,O}$, as well as the corresponding relative adsorption constants, $K_{L,O}$, were obtained at all temperatures studied. According to the results, in both of the Sepiolite supported catalysts studied, selectivity values steadily increased with temperature in the interval studied. Besides, $R_{L,O}$ and $K_{L,O}$ exhibited an Arrhenius type law with temperature that enabled us to obtain several kinetic parameters affecting the selectivity of the consecutive hydrogenation process and closely related to the electronic density of supported nickel which is modified by Ni–Cu alloying.

Keywords: Bimetallic catalysts; Sepiolite; Nickel; Copper; Supported catalysts; Ethyl linolate; Hydrogenation; Consecutive hydrogenation

1. Introduction

In previous papers we concluded that Sepiolite, a hydrous magnesium silicate: $\text{Si}_{12}\text{Mg}_8\text{O}_{32} \cdot n\text{H}_2\text{O}$ [1], could be not only an acid catalyst [2–6], an excellent support in Pd and Rh hydrogenation catalysts [7–9], but also an adequate support component [10] to enable tailored Ni–Cu catalysts to be used in oil and fat hydrogenation by taking into account its comparatively lower cost as well as the fact that the Ni–Cu alloy exhibits substantially higher selectivity than monometallic supported nickel catalysts, including some commercial catalysts also studied.

Thus, liquid-phase selective hydrogenation of ethyl linolate to ethyl oleate was carried out on nickel and Ni–Cu catalysts supported on Sepiolite as well as on several different supports. The results indicated that catalytic activity and selectivity correlated closely with some textural and/or acid–base properties of the support. Furthermore, regardless of which support was used, the highest selectivity obtained >98% was always closely related to the presence of Cu as a second metal, especially when Ni–Cu was in the proportion 20–0.3. Besides, catalytic activity was lower in bimetallic catalysts.

The present paper evaluates the role of Cu in Sepiolite-supported bimetallic Ni–Cu catalysts

^{*} Corresponding author.

through the results obtained in a kinetic study on temperature influence in the consecutive hydrogenation of ethyl linolate to ethyl oleate and ethyl stearate using the best mono and bimetallic catalysts previously described [10]. Taking into account that linoleic (*cis*-9, *cis*-12-octadecadienoic), oleic (*cis*-9-octadecenoic) and stearic (octadecanoic) acids are the major constituents of fatty acids in olive oil, this report study the potential use of these clay supported Ni–Cu catalysts in production-scale oils hydrogenation.

2. Experimental

2.1. Catalysts

The syntheses and characterization of both Ni and Ni–Cu supported catalysts used in this work were previously described [10]. A natural Sepiolite, from Vallecas (Madrid) supplied by Tolsa S.A., was as received used as support. They were as reported elsewhere [11–16] prepared by impregnation of the Sepiolite to incipient wetness with aqueous solutions of nickel or nickel and copper. Then, they were dried, crushed and screened to particle size < 0.149 mm, reduced in an ultrapure hydrogen stream ($1.7 \text{ cm}^3 \text{ s}^{-1}$) at 673 K for 3 h, and then cooled to room temperature in the same hydrogen stream.

Final metal loadings were determined by atomic absorption spectrometry and the corresponding metal surface areas were determined from the average crystallite diameter obtained by X-ray diffraction measurements assuming that nickel particles are monocrystalline [9]. Thus, Ni/Sepiolite catalyst exhibited 39.4 wt% Ni weight while Ni–Cu/Sepiolite had 18.5 wt% Ni and 0.3 wt% Cu. Their corresponding nickel surface areas were 24 and 77 ($\text{m}^2 \text{ g}_{\text{Ni}}^{-1}$), respectively.

2.2. Apparatus, materials and procedure

According to the procedure previously employed [10–16] hydrogenation runs were per-

formed in a conventional low pressure hydrogenator (Parr Instr. Co., Md. 3911) at controlled pressure and temperature conditions. Ethyl linolate and ethyl oleate (Fluka p.a.) hydrogen (99.999%, S.E.O.) and solvent methanol (99%, Panreac) were used without further purification. Most hydrogenation reactions (individual and consecutive) were carried out in 25 ml of 0.5 M methanolic solution of substrate under hydrogen pressure of 0.41 MPa with 0.3 g of catalyst and temperature range between 305 and 337 K. In order to test the lack of mass transfer limitations in the range of the operation variables studied, one set of reactions was carried out in the pressure range of 0.3–0.7 MPa, substrate concentration of 0.5–3 M and catalyst weight range of 0.05–1 g. The initial reaction rate was calculated by taking the initial slope of the plot of the hydrogen pressure decrease on the manometer versus time. The consecutive reactions were followed by GLC with FID and a column packed with 10% ethylene glycol succinate in 80/100 Chromosorb GAW-DMCS, analyzing the reaction mixtures at appropriate intervals of hydrogen uptake.

3. Results and discussion

Several hydrogenation runs, performed at various agitation regimes and with different amounts of catalysts, showed that the initial rate of hydrogenation was directly proportional to the catalyst weight and not affected by the shaking regime above 200 strokes min^{-1} so that we can assume the absence of external diffusion control. The internal diffusion was excluded by using catalysts with a enough small grain diameter, lower than 0.149 mm. Experiments carried out at standard conditions with catalysts of several grain sizes showed that reaction rates decreases when the grain size is greater than 0.21 mm so that internal diffusion limiting the rate of hydrogenation [17,18] is excluded when the grain size is lower than 0.21 mm. Thus, the kinetic data obtained in the range of the operation variables studied are free from transport influences as previously

Table 1

Temperature influence on catalytic activity and selectivity in the liquid-phase hydrogenation of ethyl linolate and ethyl oleate on Ni/Sepiolite catalyst under standard conditions

T (K)	r_L ($\mu\text{mol s}^{-1} \text{g}^{-1}$)	r_O ($\mu\text{mol s}^{-1} \text{g}^{-1}$)	$R_{L,O}$	$K_{L,O}$	S (%)
305	17.90	1.26	13.66	0.96	96.7
311	29.61	1.37	17.65	0.82	97.4
318	54.37	1.43	20.84	0.55	97.8
323	76.70	1.50	24.76	0.48	98.1
333	116.50	1.79	26.95	0.41	98.3
337	122.60	1.99	31.68	0.51	98.5

Table 2

Temperature influence on catalytic activity and selectivity in the liquid-phase hydrogenation of ethyl linolate and ethyl oleate on Ni-Cu/Sepiolite catalyst under standard conditions

T (K)	r_L ($\mu\text{mol s}^{-1} \text{g}^{-1}$)	r_O ($\mu\text{mol s}^{-1} \text{g}^{-1}$)	$R_{L,O}$	$K_{L,O}$	S (%)
305	0.19	0.16	30.44	25.63	98.5
311	0.31	0.24	32.43	25.11	98.6
318	0.49	0.35	36.05	25.75	98.7
323	0.71	0.46	37.84	24.51	98.8
333	0.92	0.62	39.47	26.60	98.8
337	1.08	0.81	41.41	31.06	98.9

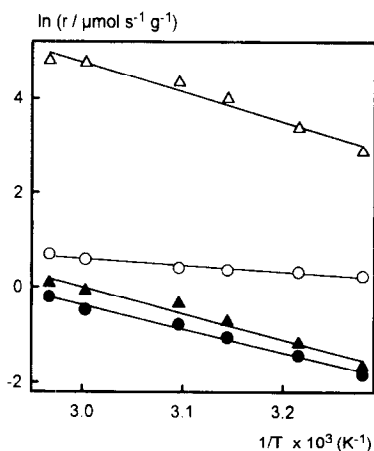


Fig. 1. Arrhenius plots for the individual liquid-phase hydrogenation under standard conditions on Ni/Sepiolite: (Δ) ethyl linolate; (\circ) ethyl oleate and on Ni-Cu/Sepiolite: (\blacktriangle) ethyl linolate, (\bullet) ethyl oleate.

obtained with several olefinic compounds [11–16] as well as with these same substrates [10]. However, at higher temperature values, a small tendency to deviation from the linear behavior in the plot of $\ln r$ vs. T^{-1} sometimes occurs, indi-

cating that at the highest temperature range, we are working in the limit of conversions where some transport limitations could be appearing.

Blank experiments over pure supported 0.7 and 24 wt% Cu catalysts did not exhibit any catalytic activity under the present experimental conditions. Furthermore, the hydrogenation rates for both substrates, ethyl linolate and ethyl oleate, under the present standard conditions at 323 K were zero order in substrate concentration as well as in hydrogen pressure in the ranges studied, so that the initial reaction rates r_L and r_O reported in Table 1 and Table 2 can be directly used as the reaction constant values to obtain (Fig. 1) the corresponding apparent activation energies, E_a , and Arrhenius constant, $\ln A$, collected in Table 3. The Eyring equation also evaluates the temperature dependence of reaction rates in terms of transition state theory by separating the enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , components. Their corresponding values, obtained by plotting $\ln rT^{-1}$ against T^{-1} , are also shown in Table 3.

In the consecutive process:

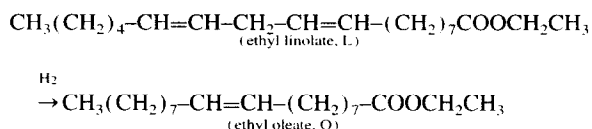
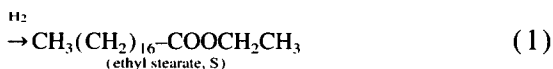


Table 3

Experimental values of activation parameters obtained from the representation of different kinetic parameters against T^{-1} . Uncertainties are determined by their respective standard deviations for a 95% confidence limit

Kinetic parameter	Activation parameter	Ni/Sepiolite	Ni-Cu/Sepiolite
$\ln r_L$	E_{aL} (kJ/mol)	52.3 ± 4.8	45.4 ± 4.1
	$\ln A_L$	9.8 ± 1.8	2.6 ± 1.6
$\ln r_O$	E_{aO} (kJ/mol)	11.6 ± 1.4	41.4 ± 2.2
	$\ln A_O$	-9.0 ± 0.5	0.8 ± 0.8
$\ln r_L/T$	ΔH_L^\ddagger (kJ/mol)	49.7 ± 4.8	42.9 ± 4.2
	ΔS_L^\ddagger (J/mol K)	-173.0 ± 9.9	-233.0 ± 9.9
$\ln r_O/T$	ΔH_O^\ddagger (kJ/mol)	8.9 ± 1.3	38.8 ± 2.2
	ΔS_O^\ddagger (J/mol K)	-329.8 ± 4.2	-248.5 ± 7.5
$\ln R_{L,O}$	$\Delta E_{(\text{true})L,O}$ (kJ/mol)	20.7 ± 2.0	8.0 ± 0.7
$\ln K_{L,O}$	$\Delta H_{L,O}^{\text{ads}}$ (kJ/mol)	-20.3 ± 5.2	3.9 ± 2.2
	$\Delta S_{L,O}^{\text{ads}}$ (J/mol K)	182.5 ± 9.9	75.4 ± 6.8



the relative reactivities of linoleic and oleic ethyl esters, $R_{L,O}$, as well as the corresponding relative adsorption constants, $K_{L,O}$, were successfully obtained by introducing a modification [7,8,15,19] into the classical Rader–Smith kinetic equation [20] of competitive hydrogenations:

$$R_{L,O} = \frac{r_L}{r_O} K_{L,O} = \log \frac{C_L^I}{C_L} / \log \frac{C_L^I}{C_L - (C_O^I - C_O)} \quad (2)$$

where C_L^I and C_O^I are concentrations of L and O when $C_L = C_O$. They are easily obtained from the point of interception (I point) of the distribution plots of the reactant and products in the course of the consecutive hydrogenation shown in Fig. 1 (a). This value $C_L^I = C_O^I$ is used instead of C_L^O and C_O^O , respectively, and is in an equimolecular proportion as C^O values are habitually employed in a competitive process [20–22]. Thus, this equation takes into account the additional concentration of O present in the reaction as a consequence of the transformation $L \rightarrow O$, which is evaluated as $C_O^I - C_O$, when there are not any secondary reactions, as obtained under the present experimental conditions.

From the results of the consecutive process shown in Fig. 2 (a), the straight line shown in Fig. 2 (b) was obtained. The values of relative reactivity, $R_{L,O}$, for both catalysts at the different temperatures studied were determined from the slopes of the straight lines obtained in their log–log plots according to Eq. (2). They are shown in Table 1 and Table 2 where $K_{L,O}$ values, obtained from $R_{L,O}$ and the corresponding individual hydrogenation rates, r_L and r_O , are also collected in Table 1 and Table 2. Besides, if we consider that both consecutive (and competitive) reactions exhibit the zero reaction order, the linearity of the plot in Fig. 2 (b) can be taken as evidence of the validity of the theoretical treatment [20–22]. Due to the fact that relative reactivity, $R_{L,O}$, is an index of the hydrogenation reactivity of linoleic ethyl ester compared to that of oleic ethyl ester, high

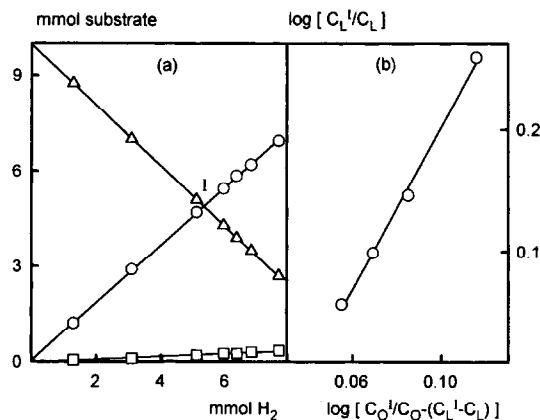


Fig. 2. Consecutive hydrogenation of ethyl linolate on Ni/Sepiolite under standard conditions at 323 K. (a) Distribution of reactant and products as a function of hydrogen consumption: (Δ) ethyl linolate, (\circ) ethyl oleate and (\square) ethyl stearate. (b) Logarithmic plot of the disappearance of ethyl linolate respect to ethyl oleate according to Eq. 2.

values of this parameter are consistent with the high selectivity, S , also shown in Table 1 and Table 2, obtained from the relative concentration of L with respect to $(O+L)$ at a very low concentration of L [23].

According to Eq. (2), $R_{L,O}$ values are determined by two components, the ratio of the initial reaction rates r_L/r_O and the relative adsorption constant values, $K_{L,O}$. In this respect, the high $R_{L,O}$ (and also S) in the Ni/Sepiolite catalyst is explained by its higher r_L/r_O value while in the bimetallic Ni–Cu/Sepiolite catalyst, it can be associated with the higher value in $K_{L,O}$. Consequently, the influence of Cu as a second metal in selectivity is closely related to its influence in the $K_{L,O}$ parameter which may be associated with metal–support interaction effects of an electronic character. In this respect, the increased $K_{L,O}$ values for the Ni–Cu alloy may be interpreted as a consequence of the increased electronic density of the Ni d-band, which may be ascribed to an electronic transfer from Cu to Ni, according to the results previously described with bimetallic Ni–Cu catalysts in the consecutive hydrogenation of propargyl alcohols [15] as well as with platinum and other Group VIII metals in the competitive hydrogenation of toluene with respect to benzene [24–26]. In this respect, for a pair of hydrocarbons

with different electronic structure, any change in the electronic structure of the surface metal sites resulted in a modification of the relative adsorption constant values, showing a higher degree of sensitivity than that obtained by using physical techniques [25,26].

The role of Cu may be better understood taking into account the changes produced in $R_{L,O}$ and $K_{L,O}$ with temperature. Thus, in both the sepiolite supported catalysts studied, selectivity values steadily increased with temperature in the interval studied (Table 1 and Table 2). Besides, $R_{L,O}$ and $K_{L,O}$ exhibited an Arrhenius type law with temperatures that let us obtain several kinetic parameters. According to Tanaka and Chihara [27], changes in $R_{L,O}$ and $K_{L,O}$ with temperature may be expressed by the relationships:

$$\begin{aligned} R \frac{d(\ln R_{L,O})}{d(1/T)} &= -(E_{aL} - E_{aO}) \\ &\quad - (\Delta H_L^{\text{ads}} - \Delta H_O^{\text{ads}}) \\ &= -(E_{aL} + \Delta H_L^{\text{ads}}) \\ &\quad + (E_{aO} + \Delta H_O^{\text{ads}}) \\ &= -\Delta E_{(\text{true})L,O} \end{aligned} \quad (3)$$

$$R \ln K_{L,O} = \Delta S_{L,O}^{\text{ads}} - \Delta H_{L,O}^{\text{ads}} T^{-1} \quad (4)$$

where R is the gas constant, $\Delta S_{L,O}^{\text{ads}}$ and $\Delta H_{L,O}^{\text{ads}}$ are, respectively, the differential entropy and differential adsorption heat (or enthalpy, negative values for exothermic) of adsorption between ethyl linolate and ethyl oleate on the catalyst surface. Taking into account that E_a , apparent activation energies, is the energy required for bringing a substrate in the bulk solution up to the activation state on the catalyst surface, the quantity $(E_a + \Delta H^{\text{ads}})$ represents the energy required for bringing the adsorbed substrate to the activated state or 'true activation energy'. Besides, while in an individual zero-order hydrogenation reaction all active sites are occupied by the reactant molecules [28], in a competitive (or consecutive) hydrogenation process the whole surface active sites are also occupied but by both reactants (O

or L, in the present case) in the proportion corresponding to the $R_{L,O}$ value [29,30].

In this respect, according to the results previously obtained [14,15], we find that the dependence of $R_{L,O}$ on temperature is determined by the difference between the true activation energy of the two substrates, $\Delta E_{(\text{true})L,O}$. All these activation parameters obtained from Eqs. (3) and (4) are collected in Table 3. According to these results, we have to remark on the coincidental results obtained between the values of $\Delta E_{(\text{true})L,O}$ directly obtained from the slope of the Arrhenius plot in Eq. (3) and those from E_a and $\Delta H_{L,O}^{\text{ads}}$ calculated by the derived expression of Eq. (3):

$$(E_{aL} - E_{aO}) + \Delta H_{L,O}^{\text{ads}} = \Delta E_{(\text{true})L,O} \quad (5)$$

Values of 20.4 and 7.9 (kJ/mol) thus obtained, for Ni/Sepiolite and Ni-Cu/Sepiolite, are very close to the 20.7 and 8.0 collected in Table 3.

On the other hand, the electronic influence of Cu promoting such an important change in the differential adsorption heat of the two substrates, $\Delta H_{L,O}^{\text{ads}}$, ought to be considered as being mainly responsible for the selectivity improvement promoted by the addition of this element to supported nickel catalysts because it is this adsorption kinetic parameter that experiments the highest change. Thus, negative value for $\Delta H_{L,O}^{\text{ads}}$ indicates that $\Delta H_L^{\text{ads}} < \Delta H_O^{\text{ads}}$ in Ni/Sepiolite while the opposite is true in Ni-Cu/Sepiolite, considering the positive value obtained for this parameter. Thus, taking into account that enthalpy negative values indicate an exothermic process, ethyl linolate is adsorbed more strongly than ethyl oleate in Ni/sepiolite. The electronic influence of the Ni-Cu alloy promotes the strongest adsorption of ethyl oleate. Besides, changes obtained in differential entropy values, $\Delta S_{L,O}^{\text{ads}}$, are comparatively less important.

According to the results, we may conclude that by using $R_{L,O}$ and $K_{L,O}$ parameters obtained at different temperatures, it is possible to obtain valuable information concerning parameters affecting the selectivity of the consecutive hydrogenation process and closely related to the electronic density (or level) of supported nickel

which is modified by Ni–Cu alloying. Thus, on the basis of these results and according to previous papers [15,19], an increase in electronic density in supported nickel promotes a variable increase in $K_{L,O}$ joined to a variable decrease in r_L/r_O .

Finally, we have also to conclude that Cu addition to a supported Ni catalyst promote changes in catalytic activity and selectivity due to the influence of Ni–Cu alloying in the electronic structure of the Ni d-band as well as in the ‘ensemble effect’, associated with the geometric structure of active sites. The former would be associated with changes in enthalpy parameters such as $\Delta H_{L,O}^{\text{ads}}$, while the latter will be better related to changes in entropy ones such as $\Delta S_{L,O}^{\text{ads}}$. Thus, taking into account the important changes obtained in $\Delta H_{L,O}^{\text{ads}}$ values by the Ni–Cu alloying with respect to those obtained in $\Delta S_{L,O}^{\text{ads}}$, results obtained here are more in agreement with the viewpoint of Burch [31] or Somorjai [32] than with the opinion of Ponec [33,34] or Martin [35] with respect to the prevailing role of electronic against geometric or ensemble effects in determining the catalytic behavior of Ni–Cu bimetallic alloys.

However, the decrease of activity obtained in Table 1 and Table 2 when Cu is added to Ni can be therefore accounted for primarily in terms of geometric or ensemble effects, assuming an important decrease in the number of active sites on nickel surface associated to the production of different structural defects on nickel crystallites. These structural defects of supported-nickel crystallites such as ‘twin faults’, ‘stacking faults’ and ‘microstrains’ were obtained by X-ray diffraction line broadening analysis in a previous work [19]. According to the clearly different ΔH^{\ddagger} values for L and O, Ni/Sepiolite could have two kinds of active sites with different electronic density. Cu addition seems to avoid the action of the most active ones, according to the similar values of ΔH^{\ddagger} (and E_a) in L and O in Ni–Cu catalyst, both also nearly coincidental with ΔH_L^{\ddagger} in Ni catalyst. This drastic reduction in the number of active sites is also responsible of the important decrease in r_L and r_O values. However, only identical values of

ΔH^{\ddagger} (and E_a) could be explained by a ‘pure’ topological or ensemble hypothesis, because in such a case, it is obtained a variable reduction in the number of active sites but its energetic is not changed at all. Differences obtained in ΔH^{\ddagger} (and E_a) must be associated to electronic Ni–Cu interaction effects. Thus, Ni–Cu alloying as well as metal support interaction effects may be explained within the framework of a simultaneous action of electronic and structural or geometric effects.

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