JOURNAL OF CATALYSIS 125, 171–186 (1990)

# $AlPO_4$-Supported Nickel Catalysts

## IX. Liquid-Phase Selective Hydrogenation of Propargyl Alcohols

F. M. BAUTISTA, J. M. CAMPELO, A. GARCIA, R. GUARDEÑO, D. LUNA, AND J. M. MARINAS

*Department of Organic Chemistry, University of Cordoba, E-14004 Cordoba, Spain*

Received June 21, 1989; revised March 20, 1990

The liquid-phase consecutive hydrogenation of propargyl alcohols (2-propyn-1-ol, 3-butyn-2-ol, and 2-methyl-3-butyn-2-ol) has been carried out at 293–323 K and in an initial hydrogen pressure range of 0.3–0.7 MPa on three nickel catalysts at 20 wt% supported on two different types of $AlPO_4$. A bimetallic Ni–Cu catalyst was also employed as a catalyst. Furthermore, individual hydrogenation of related allyl alcohols was carried out under identical experimental conditions. Thus, by introducing a modification in the classical kinetic equation of competitive hydrogenations, the relative reactivities $R_{D,T}$ as well as the relative adsorption constants $K_{D,T}$ were successfully obtained in the consecutive process. The independence of $R_{D,T}$ with respect to the temperature and the Arrhenius-type law obtained from ln $K$ vs $T^{-1}$ was ascribed to the existence of a linear free-energy relationship (LFER) which also manifested itself in the existence of a linear correlation between the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (and between $E_a$ and ln $A$) known as the "compensation effect." On the basis of these results, valuable information was obtained concerning not only the mechanism of the liquid-phase catalytic hydrogenation of propargyl alcohols but also the parameters affecting the selectivity of the process.

## INTRODUCTION

Catalytic semihydrogenation of alkynes to Z-alkenes is not only a very important synthetic operation (*1*) but is also of industrial interest. For instance, some fundamental chemical processes require large amounts of olefins of reagent-grade purity with a very low alkyne content. Actually, this latter requirement is fulfilled in part by the half-hydrogenation of alkynes in fluxing systems with chromium–nickel, Pd on silica, or cobalt molybdate catalysts (*2*). Furthermore, butenediol, obtained by the liquid-phase semihydrogenation of butynediol, is a raw material for insecticides and vitamin $B_6$ (*3*) while isophytol, a key step in the synthesis of vitamin E, is also obtained by liquid-phase hydrogenation of dehydroisophytol or 3,7,11,15-tetramethyl-1-hexadecyn-3-ol (*4*). Similarly, 2-methyl-3-butyn-2-ol is an intermediate for an industrial synthesis of isoprene (*5*).

As can be seen, many compounds related to the propargyl alcohol structure are of both theoretical and practical interest (*3–7*). Therefore, it is sometimes used as a probe molecule for the selective semihydrogenation of the acetylenic bond (*8, 9*).

As a continuation of our work on the catalytic activity of $AlPO_4$-supported nickel catalysts (*10–16*), the present paper reports on the results of the liquid-phase catalytic semihydrogenation of propargyl alcohol (P-yn, 2-propyn-1-ol) and its two methyl derivatives (B-yn, 3-butyn-2-ol) and (MB-yn, 2-methyl-3-butyn-2-ol). Furthermore, hydrogenation reactions of related allyl alcohols (P-en, 2-propen-1-ol), (B-en, 3-buten-2-ol), and (MB-en, 2-methyl-3-buten-2-ol) are also studied separately under the same experimental conditions. Thus, not only the sup-

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TABLE 1

Textural and Acid–Base Properties of Supports

| Support | $S^{a}_{\mathrm{BET}}$ ($m^2\ g^{-1}$) | $S^{b}_{t}$ ($m^2\ g^{-1}$) | $V^{c}$ ($ml\ g^{-1}$) | $d^{d}$ (nm) | Acidity[e] ($\mu mol\ g^{-1}$) | Basicity[f] ($\mu mol\ g^{-1}$) |
|---|---|---|---|---|---|---|
| $AlPO_4$-P | 228 | 236 | 0.94 | 2–4 | 180 | 80 |
| $AlPO_4$-NP | 6 | — | — | — | 10 | —[g] |

[a] Surface area, determined from BET method.

[b] Surface area from $V$–$n$ plots.

[c] Pore volume.

[d] Main pore diameter.

[e] Monolayer coverage $X_m$ at equilibrium at 298 K obtained with pyridine ($pK_a = 5.25$).

[f] Monolayer coverage $X_m$ at equilibrium at 298 K obtained with acrylic acid ($pK_a = 4.25$).

[g] There is no adsorption of titrant agent.

port effects but also those of methyl substitution can be compared with respect to the selectivity and catalytic activity of triple-bond hydrogenation versus that of alkene.

## EXPERIMENTAL

### *Supports*

Aluminum orthophosphates prepared according to Kearby (*17*) have been obtained by precipitation with propylene oxide from aqueous solutions of $AlCl_3 \times 6H_2O$ and $H_3PO_4$ at 85 wt%, pH 6.1, at the "precipitation endpoint." The resulting solid with a composition of $Al/P = 1$ was washed with isopropyl alcohol, dried at 393 K for 24 h, and then screened to <0.149 nm. Two different supports were obtained when this solid was calcined for 3 h in an electric muffle furnace at 920 or 1070 K. References to these supports will be made by $AlPO_4$-P for the former and $AlPO_4$-NP for the latter, indicating their respective porous and nonporous characteristics shown in Table 1. These textural properties (surface area, pore volume, and main pore diameter), determined by nitrogen adsorption, and the detailed synthesis procedure as well as the surface basicity and acidity of supports, have been published elsewhere (*11, 18*). Acid–base properties, also collected in Table 1, were determined by a spectrophotometric method described elsewhere (*19–21*) that allows titration of the amount of irreversibly adsorbed acrylic acid ($pK_a = 4.2$) or pyridine ($pK_a = 5.25$) employed as titrant agents of basic and acid sites, respectively. The monolayer coverage at equilibrium at 298 K, $X_m$, is accomplished by applying the Langmuir adsorption isotherm, and it is assumed to be a measure of the acid or basic sites corresponding to the specific $pK_a$ of the base or acid used as the titrant.

### *Catalysts*

The synthesis of Ni-supported catalysts was carried out as previously reported (*10, 11*). Catalysts containing 20 wt% nickel were prepared by impregnation of both supports to incipient wetness with 10 $M$ aqueous solutions of nickel nitrate. They were dried, crushed, and screened to particle size <0.149 (100 mesh size), reduced in an ultrapure hydrogen stream (100 ml $min^{-1}$) at 673 K for 3 h, and finally cooled to room temperature in the same hydrogen stream.

Similarly, another 20 wt% nickel catalyst was prepared identically using an $AlPO_4$-P modified by ethylenediaminetetraacetic acid (EDTA) according to the method described by Barcicki *et al.* (*22*). Impregnation of the support with the modifier was carried out at 345 K with an 0.05 $M$ aqueous solution of EDTA (Merck, p.a.) (5 ml $g^{-1}$ of support) and vigorously stirred for 20 min. The modified support was dried at 393 K for 24 h before impregnation to incipient wetness with nickel nitrate like the former catalysts.

A bimetallic Ni–Cu catalyst supported on $AlPO_4$-P was also synthesized by coimpregnation to incipient wetness with 10 *M* aqueous solutions of nickel nitrate and copper nitrate in a proportion that attained 20 wt% nickel and 0.3 wt% copper. The resulting powder was reduced in the hydrogen stream under the above experimental conditions.

### *Dispersion Measurements*

Metal surface areas, $S$, for different catalysts were determined from the average crystallite diameter $D$, obtained by the X-ray diffraction technique (XRD) according to the method of Moss (*23*) as has been described elsewhere (*10–16*).

The crystallite sizes were determined by X-ray line broadening using a Philips Model 1103/00/60 diffractometer with Fe-filtered Co$K\alpha$ radiation. A scan speed of 7.5° $h^{-1}$ was used for the $2\theta$ range between 46° and 56° for the determination of $D$ values from the width of the (111) nickel peak at half the maximum peak height. Instrumental broadening correction was made using the Warren equation (*24*), where the experimental width $B$ is corrected from an instrumental factor, $b$, obtained by using a quartz reference sample (100 nm $< D <$ 1000 nm), taken equal to 0.2°. All XRD runs were carried out on powder samples of catalysts; Table 2 summarizes the average crystallite diameter, $D$, and metal surface area, $S$, of different supported nickel catalysts.

Table 2 also shows results obtained in hydrogen chemisorption experiments. They were performed using a conventional Pyrex glass volumetric adsorption apparatus (*23, 25*). The previously reduced catalyst sample (1 g) was activated *in situ* under hydrogen at 673 K for 2 h, after which the apparatus was evacuated for 1 h and filled with helium for 2 h while the sample was maintained at the final activation temperature. Finally, at this temperature the sample was evacuated for 1 h and then cooled to room temperature under vacuum.

Hydrogen adsorption isotherms were measured at 298 K, allowing 0.5 h at each point for the attainment of equilibrium. The pressure range used for chemisorption was 10–90 KPa. The apparent dispersions were determined by assuming monolayer coverage (H/Ni = 1) and spherical particles with an equal distribution of the three lowest nickel index planes (*26*). Blank experiments determined that hydrogen chemisorption on the supports was negligible within the uncertainty of the measurements.

Assuming spherical metal crystallites all having the same size, $D$, the apparent dispersion values may be obtained from average crystallite diameters, $D$, obtained from XRD (*26*) by

$$\text{apparent dispersion (\%)} = 97.1/D\ \text{(nm)}.$$

By dividing the values of apparent dispersion obtained from chemisorption measurements by those so determined from XRD data, we obtain the fraction of surface nickel atoms, $X$, that are able to chemisorb hydrogen molecules. Thus, this fraction is also a measure of the surface density of metal active sites for hydrogen chemisorption.

### *Apparatus, Materials, and Procedure*

According to the procedure previously employed (*10–15*), hydrogenation runs were carried out in a closed vessel using vigorous shaking (300 strokes $min^{-1}$) in a conventional low-pressure hydrogenator (Parr Instrument Co., MD., 3911) furnished with a manometer whereby the actual pressure in the isolated reaction vessel (500 ml) was constantly monitored. The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket, with an accuracy of ±0.5 K.

The chromatographically pure alcohols (2-propyn-1-ol, 3-butyn-2-ol, 2-methyl-3-butyn-2-ol, 2-propen-1-ol, 3-buten-2-ol, and

TABLE 2

Average Crystallite Diameter, *D*, and Metal Surface Area, *S*, from X-Ray Measurements, Hydrogen Chemisorption Results, and Fraction of Surface Nickel Atoms Able to Hydrogen Chemisorption, *X*, in Supported Nickel Catalysts

| Catalysts | X-ray measurements | | | Hydrogen chemisorption | | *X* |
|---|---|---|---|---|---|---|
| | *D* (nm) | *S* ($m^2\ g_{Ni}^{-1}$) | Apparent dispersion (%) | Hydrogen uptake ($\mu mol\ g^{-1}$) | Apparent dispersion (%) | |
| Ni/$AlPO_4$-P | 21 | 32 | 4.62 | 17.9 | 1.05 | 0.23 |
| Ni/$AlPO_4$-NP | 37 | 18 | 2.62 | 9.4 | 0.55 | 0.21 |
| Ni/$AlPO_4$-P(EDTA) | 7 | 96 | 13.87 | 29.7 | 1.74 | 0.11 |
| Ni/$AlPO_4$-P(Cu) | 10 | 65 | 9.71 | 179.1 | 10.50 | 1.08 |

2-methyl-3-buten-2-ol) were used as supplied commercially (Merck, p.a.) after distillation under reduced pressure and low temperature. Then they were passed through active acidic aluminum oxide powder for chromatography (Merck) which was activated at 673 K in flowing ultrapure nitrogen. Methanol (p.a. 99% Panreac) employed as solvent and hydrogen (99.999%, SEO) were used without further purification.

Most hydrogenation reactions (individual and consecutive) were carried out in 25 ml of 1 *M* methanolic solution of substrate, at 313 K under initial hydrogen pressure of 0.41 MPa with 0.3 g of catalyst. One set of reactions was carried out with the catalyst Ni/$AlPO_4$-P in the hydrogen pressure range 0.3–0.7 MPa, the temperature range 293–323 K, the substrate concentration range 0.5–3 *M*, and the catalyst weight range 0.3–1 g in order to test the influences of initial hydrogen pressure, temperature, substrate concentration, and diffusion control on the catalytic activity and selectivity in the consecutive hydrogenation of propargyl alcohols. Individual hydrogenation of allyl alcohols was also studied under the above experimental conditions with Ni/$AlPO_4$-P catalyst.

The initial reaction were calculated by taking the initial slope of the plot of the hydrogen pressure decrease at the manometer versus time. As these plots were always practically linear (Fig. 1), the determination was straightforward and reproducible to within about 6%. The areal rate, $r_A$, defined as the activity per unit surface area of nickel metal in mol $s^{-1}$, $m_{Ni}^{-2}$, was obtained from the initial reaction rate and the metallic surface area (*S*) of the catalysts.

The consecutive reactions were followed by GLC analyzing the reaction mixtures at appropriate intervals of hydrogen uptake. GLC analyses were performed with a Hewlett–Packard 5830 gas chromatograph fitted with an H.P. 18850 GC terminal, equipped with a column packed with 5% escualane for allyl alcohols and with 5% carbowax-20M for propargyl alcohols, both in 80/100 Chromosorb GAW-DMCS. Neither isomerization nor hydrogenolysis products were detected in any of the cases.

## RESULTS AND DISCUSSION

According to *X* values in Table 2, all the catalysts with the exception of Ni/$AlPO_4$-P(Cu) exhibited a loss in the expected hydrogen chemisorption capacity, in agreement with the results of Marcelin *et al.* (*27–29*), who obtained changes in chemisorptive properties and in magnetic behavior when nickel was supported on a phosphate-containing support. This behavior was ascribed to effects of a strong

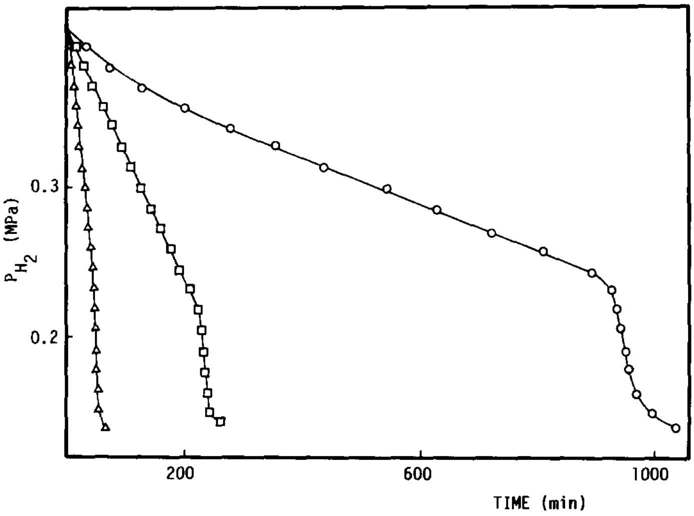

FIG. 1. Dependence of hydrogen pressure on time for the consecutive hydrogenation of 2-propyn-1-ol (○), 3-butyn-2-ol (□), and 2-methyl-3-butyn-2-ol (△) with 0.3 g of Ni/AlPO$_4$-P at 313 K.

metal–support interaction effect (SMSI) caused by the formation of a bulk alloy with P (*28*).

In fact, the results for apparent dispersion collected in Table 2 are very similar to those described for nickel catalysts supported on $Al_2O_32AlPO_4$ and $4MgO13Al_2O_310AlPO_4$ at the same metal loading and reduction temperature (*27, 28*), in accordance with the highest P/Ni ratio. In this respect, they also obtained a lowering in hydrogen uptake on decreasing metal loadings. We had also previously obtained similar behavior with areal rates of Ni/AlPO$_4$ catalysts in the liquid-phase hydrogenation of 1-hexene (*10, 11*).

On determining $X$ values as the quotient between apparent dispersion from hydrogen chemisorption and from XRD data, we assume that the later give us a reasonably good measure of the actual apparent dispersion while the former, due to SMSI effects, only provides a relative value of metal surface atoms able to chemisorb hydrogen molecules. This assumption is supported by the reasonable close agreement between the dispersion values obtained from XRD and chemisorption experiments (9.7 and 10.5, respectively) in Ni/AlPO$_4$-P(Cu) catalyst. Thus, values of $X$ in Table 2 express not only values of surface density of active nickel atoms in hydrogen chemisorption but also may be considered a measure of the extension of SMSI effects in AlPO$_4$-supported nickel catalysts. Moreover, according to these results, the presence of Cu as a second metal in the catalyst Ni/AlPO$_4$-P(Cu) seems to avoid SMSI effects because its surface density, $X \simeq 1$, indicates that all the surface nickel atoms are active in hydrogen chemisorption.

These facts take into account the existence of SMSI effects closely related to the P/Ni ratio in catalysts where Ni is supported on phosphorous-containing materials. Consequently, the method of Madon and Boudart (*30*), based on the use of different metal loadings, to test the nonexistence of internal or external transport limitations cannot be used in these cases because the metal loading may affect $r_A$ values independently of the potential mass transfer influences. Owing to this, we have followed the criterion of Satterfield (*31*), also used by Boudart *et al.* (*32*), based on the determination of the limit of grain size where internal diffusion control operated.

Thus, in order to avoid internal and external hydrogen diffusion control, the selected working conditions are the same as those determined in previous work (*15*) for the liquid-phase individual and competitive hydrogenation of allyl alcohols (2-propen-1-ol, 2-methyl-2-propen-1-ol, and 2-buten-1-ol) with the Ni/$AlPO_4$-P catalyst. Internal diffusion control was only found to operate when the grain size was greater than 0.21 mm. Consequently, the potential interference of internal diffusion is avoided by using catalysts sieved down to 0.149 mm. Moreover, the effect of external diffusion was checked by lowering the shaking regime from 300 to 100 strokes $min^{-1}$. The reaction rates were independent of the agitation speed over 200 strokes $min^{-1}$ as previously obtained with several olefinic compounds (*10–15*).

On the other hand, the hydrogen uptake rate, $r$, in the hydrogenation of 2-methyl-3-butyn-2-ol under standard conditions was found to be linearly related to the weight of the Ni/$AlPO_4$-P catalyst used, $w$. The plot of $r^{-1}$ versus $w^{-1}$ was also linear, and from the inverse of the interception at origin (*31*), a hydrogen transfer rate of $0.21 \times 10^{-3}$ mol $s^{-1}$ was obtained. Thus, all the reactions exhibit a hydrogen uptake rate 10–12 times lower than this limit, similar to results previously obtained for allyl alcohols (*15*) with Ni/$AlPO_4$-P catalyst. These results indicated that the reaction rates are controlled by the chemical step and that the kinetic data obtained in the range of the studied operation variables are free from transport influences.

Under the present standard conditions at 313 K, the reaction order in the initial hydrogen pressure determined between 0.3 and 0.7 MPa and in the substrate concentration in the range 0.5–3 $M$ was zero order for all three propargyl alcohols as well as for the corresponding allyl alcohols studied. Consequently, identical kinetic behavior is found in the liquid-phase hydrogenation of double and triple bonds. Similar behavior was obtained in the liquid-phase catalytic hydrogenation of the olefinic double bond of several substrates on Ni/$AlPO_4$ catalysts (*10–15*) as well as on Pd/$AlPO_4$ (*33*). However, Rh/$AlPO_4$ in the hydrogenation of allyl alcohol under the present conditions gave 1.4 as the reaction order in initial hydrogen pressure (*34*), much higher than those typically obtained with this catalyst for a number of olefins (*35–37*). The reaction order in the substrate concentration was found to be $-0.5$, lower than the zero order obtained for other substrates when the same catalyst was used (*35–37*). In addition, Rh/$AlPO_4$ catalysts enabled us to achieve 100% selectivity in the reduction of the double bond of olefins, bearing a variety of organic functions (*35–37*) with neither C–N nor C–O bond hydrogenolysis nor carbonyl group hydrogenation. However, methyl-substituted allyl alcohols (*34*) yielded the side reaction product corresponding to the isomerization of the double bond to the corresponding aldehyde or ketone in addition to the expected hydrogenated compounds. In contrast, the only products detected in the liquid-phase catalytic hydrogenation of allyl alcohols with the Ni/$AlPO_4$ catalysts are the corresponding saturated alcohols. Moreover, we must also point out the absence of isomerization products in the semihydrogenation of the propargyl alcohols studied.

According to the results summarized in Table 3, we can conclude that the calcination temperature of the $AlPO_4$ support to obtain $AlPO_4$-P and $AlPO_4$-NP does not produce important changes in the catalytic activity of supported nickel. Also, SMSI effects obtained from the decrease in the hydrogen chemisorption capacity (low values of $X$ in Table 2) do not imply low $r_A$ values. However, the modification of $AlPO_4$-P with EDTA clearly decreases $r_A$ values, which in this case are associated with the highest SMSI effects (the lowest values of $X$). On the other hand, while the effects of Cu are not important in propargyl

TABLE 3

Areal Rates, $r_A$, of Different Catalysts in the Hydrogenation of Propargyl and Allyl Alcohols under Standard Conditions of 313 K and 0.41 MPa of Initial Hydrogen Pressure

| Catalysts | $r_A$ (mol s$^{-1}$ m$_{Ni}^{-2}$) × $10^6$ | | | | | | $r_D/r_T$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | P-yn | B-yn | MB-yn | P-en | B-en | MB-en | P | B | MB |
| $Ni/AlPO_4$-P | 0.25 | 1.90 | 8.05 | 40.74 | 19.73 | 15.77 | 163 | 10 | 2 |
| $Ni/AlPO_4$-NP | 0.15 | 1.47 | 8.20 | 46.85 | 17.96 | 23.38 | 312 | 12 | 3 |
| $Ni/AlPO_4$-P(EDTA) | 0.08 | 1.06 | 4.06 | 11.13 | 4.63 | 5.45 | 139 | 4 | 1 |
| $Ni/AlPO_4$-P(Cu) | 0.15 | 2.01 | 6.13 | 17.42 | 6.84 | 8.99 | 116 | 3 | 1 |

alcohols, it promotes an appreciable lowering in the specific reaction rates for allyl alcohols. In addition, this bimetallic Ni–Cu catalyst exhibits optimum activity per unit weight of supported nickel, directly obtained by the $S \times r_A$ product. These differential behaviors, also exhibited in its highest hydrogen chemisorption capacity associated to the nonexistence of SMSI effects ($X \simeq 1$), may be of interest in order to enhance the selectivity toward the allyl alcohols obtained from the semihydrogenation of the corresponding propargyl alcohols. Finally, according to the present results, we may conclude that for supported nickel catalyst the existence of SMSI effects cannot be automatically associated with a lowering of the catalytic activity of the hydrogenation reactions.

### *Consecutive Hydrogenations*

Competitive hydrogenation has been used widely to establish a structure–reactivity relationship for alkenes and other substrate (*38–40*). According to the classical Rader–Smith relation (*41*), the selectivity in the competitive hydrogenation of two compounds is determined by the relative reactivity $R_{A,B}$ as an index of the reactivity of $A$ compared to that of $B$ according to the equation

$$R_{A,B} = \frac{r_A}{r_B} K_{A,B} = \log \frac{C_A^o}{C_A} \Big/ \log \frac{C_B^o}{C_B}, \quad (1)$$

where $r_A$ and $r_B$ are respectively the initial rates of $A$ and $B$, $K_{A,B}$ is the relative adsorption constant of $A$ with respect to $B$ and may be used as a measure of the relative strength of adsorption, and $C_A$, $C_B$, $C_A^o$, and $C_B^o$ represent the actual and initial concentrations of $A$ and $B$, respectively. This expression assumes the validity of the Langmuir–Hinshelwood kinetics and considers the surface reaction to be the rate-determining step.

At the present time, Eq. (1) has been suitably employed with different pairs of substances except for the consecutive alkyne–olefin processes or diene–olefin systems (*42*). This failure was associated with the difficulty in determining $C_B^o$ values in the consecutive reactions, T → D → S, where T, D, and S represent a triple, a double, and a single carbon–carbon bond, respectively. However, in order to determine the kinetic parameters $R_{T,D}$ and $K_{T,D}$ in these processes, some research (*43*) has been carried out using the equation

$$R_{D,T} = \frac{C_D^{(max)}}{C_T^{(max)}} = \frac{r_D}{r_T} K_{D,T}, \quad (2)$$

where $C_D^{(max)}$ and $C_T^{(max)}$ are the concentrations of the components D and T at the maximum concentration of the intermediate D. This approximation to Eq. (1) takes into account the relatively strong adsorption of T compounds on catalysts with respect to D. Equation (1) has also been employed with very closely related T and

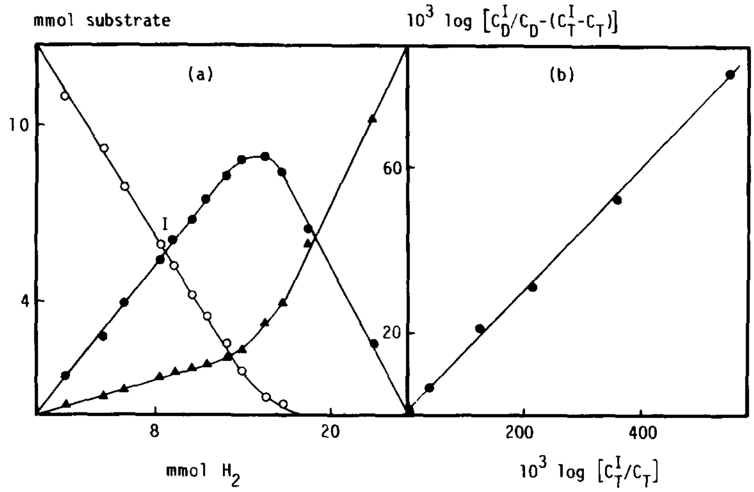

FIG. 2. Consecutive hydrogenation of 2-propyn-1-ol on Ni/AlPO$_4$-P catalyst at 313 K and under standard experimental conditions. (a) Distribution of reactant and products as a function of hydrogen consumption: (○) 2-propyn-1-ol, (●) 2-propen-1-ol, (▲) 1-propanol. (b) Logarithmic plot of the disappearance of allyl alcohol vs propargyl alcohol according to Eq. (3).

D pairs, which are 2-octyne and 1-heptene (*44*).

In the present work we are introducing a modification in Eq. (1) which lets us extend it to the consecutive processes

$$R_{D,T} = \frac{r_D}{r_T} K_{D,T} = \log \frac{C_D^I}{C_D - (C_T^I - C_T)} \Big/ \log \frac{C_T^I}{C_T}, \quad (3)$$

where $C_T^I$ and $C_D^I$ are concentrations of T and D when $C_T = C_D$. They are very easily obtained from the interception (I point) of the distribution plots of the reactant and products in the course of the consecutive hydrogenation (Fig. 2a). This value, $C_D^I = C_T^I$, is used instead of $C_D^\circ$ and $C_T^\circ$, respectively, and is in an equimolecular proportion as $C^\circ$ values are habitually employed.

Equation (3) also takes into account the additional concentration of D present in the reaction as a consequence of the transformation T → D, which may be evaluated as $C_T^I - C_T$, when there are not any secondary reactions, as obtained under the present experimental conditions. It is also convenient to determine the limit for the use of $C_D$ and $C_T$ values where they are $C_D^{(\max)}$ and $C_T^{(\max)}$, respectively.

From the results of the consecutive hydrogenation shown in Fig. 2a, we obtained the straight line shown in Fig. 2b. The values of relative reactivity, $R_{D,T}$, for all catalysts with the three alkynes studied have been determined from the slopes of the straight lines obtained in their log–log plots, in the interval between $C^I$ and $C_D^{(\max)}$, according to Eq. (3). The linearity of these plots was taken as evidence of the validity of the theoretical treatment (*38–44*).

The results thus obtained are summarized in Table 4 where $K_{D,T}$ values are also shown. These $K_{D,T}$ values were calculated from $R_{R,T}$ and the corresponding individual reaction rates, collected in Table 3. According to the method (*41*), $K$ values ought to be obtained from rate constant values, but taking into account the zero-order kinetics obtained with respect to the substrate concentration as well as with respect to the hydrogen pressure, $r_A$ values can be practically considered (and consequently used) as specific reaction rate constants.

The low values of $R_{D,T}$ shown in Table 4 are consistent with the high selectivity obtained (70–80%) with all catalysts in the semihydrogenation of propargyl alcohols to the corresponding allyl derivatives. Moreover, according to Eq. (3), $R_{D,T}$ values are determined by two factors, the ratio of the initial reaction rates $r_D/r_T$ and the relative adsorption constant values, $K_{D,T}$. According to the results, the low values of $R_{D,T}$, in spite of the high $r_D/r_T$ values, are due to the low values of $K_{D,T}$. Thus, high selectivity ought to be associated with the relatively high adsorptivity of alkynes compared to that of olefins, owing to which the latter are hydrogenated only after all starting substrate has been taken up (*42*).

On the other hand, catalyst influences in both parameters $r_D/r_T$ and $K_{D,T}$ are clearly obtained from the sequences Ni/AlPO$_4$-NP > Ni/AlPO$_4$-P > Ni/AlPO$_4$-P(EDTA) > Ni/AlPO$_4$-P(Cu) in the former parameter and exactly the opposite in the latter. Methyl substitution operates similarly; while $K_{D,T}$ values increase in the order MB-yn > B-yn > P-yn, $r_D/r_T$ values decrease following the same sequence. Thus, the compensation between the two parameters ($r_D/r_T$ and $K_{D,T}$) for each catalyst and each substrate determines the very close $R_{D,T}$ values obtained and, consequently, the narrow selectivity (70–80%) gap.

In this respect, the relative adsorption constant of toluene with respect to benzene, $K_{T,B}$, determined from a kinetic analysis of the competitive hydrogenation of these hydrocarbons, was used to probe the electronic structure of platinum and other Group VIII metals (*45–48*). Thus, for a pair of hydrocarbons with different electronic structures, any change in the structure of the surface sites resulted in a modification of $K_{T,B}$; since the toluene molecule is more of an electron donor than the benzene molecule, then the larger the electron acceptor properties of platinum surface atoms, the larger the $K_{T,B}$ values. Moreover, the modification of the electronic structure due to environmental effects (support acidity, electric field of cation adsorbates, or Pt-Zr alloys) was monitored with a higher degree of sensitivity than that obtained by using physical techniques (*46–48*). Thus, $K_{T,B}$ values decrease linearly with the decreasing Pt *d*-electron population. Consequently, methyl substitution in unsaturated alcohols operates in the same way as that in toluene by increasing the donor–acceptor interaction with the metal surface and increasing $K_{D,T}$ values. The increased $K_{D,T}$ 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 as-

TABLE 4

Relative Reactivities, $R_{D,T}$, and Relative Adsorption Constants, $K_{D,T}$, for the Consecutive Hydrogenation of 2-Propyn-1-ol, 3-Butyn-2-ol, and 2-Methyl-3-butyn-2-ol on Different Catalysts at 313 K and 0.41 MPa of Initial Hydrogen Pressure

| Catalysts | | P-en/P-yn | B-en/B-yn | MB-en/MB-yn |
|---|---|---|---|---|
| Ni/AlPO$_4$-P | $R_{D,T}$ | 0.151 | 0.248 | 0.181 |
| | $K_{D,T} \times 10^3$ | 0.918 | 23.840 | 92.430 |
| Ni/AlPO$_4$-NP | $R_{D,T}$ | 0.141 | 0.287 | 0.141 |
| | $K_{D,T} \times 10^3$ | 0.458 | 23.500 | 49.420 |
| Ni/AlPO$_4$-P(EDTA) | $R_{D,T}$ | 0.181 | 0.260 | 0.181 |
| | $K_{D,T} \times 10^3$ | 1.241 | 59.360 | 134.720 |
| Ni/AlPO$_4$-P(Cu) | $R_{D,T}$ | 0.168 | 0.287 | 0.195 |
| | $K_{D,T} \times 10^3$ | 1.463 | 84.520 | 132.820 |

cribed to an electronic transfer from Cu to Ni. Thus, the results here obtained are more in agreement with the viewpoint of Burch (*50*) or Somorjai (*51*) than with the opinion of Ponec (*49*) with respect to the prevailing role of electronic against geometric or ensemble effects in determining the catalytic behavior of bimetallic alloys.

In a series of experiments carried out in a range of initial hydrogen pressure between 0.3 and 0.7 MPa and of substrate concentrations between 0.5 and 3 $M$, relative reactivity, $R_{D,T}$, was found to be independent of the initial hydrogen pressure as well as of the substrate concentration. As a consequence of the independence of $r_A$ values with respect to these parameters under the selected conditions, differences obtained in $K_{D,T}$ are also within the experimental error.

The results obtained by studying the evolution of Ni/AlPO$_4$-P catalytic activity with temperature are collected in Tables 5 and 6. The values of the apparent activation energy, $E_a$, and the preexponential factor, ln $A$, obtained from the Arrhenius expression by plotting ln $r_A$ vs $T^{-1}$, are collected in Table 7. In this respect, the Eyring equation also evaluates the temperature dependence of reaction rates in terms of the transition state theory by separating the enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, components. Their corresponding values obtained by plotting ln $r_A T^{-1}$ vs $T^{-1}$ are also shown in Table 7. As can be seen from the values in Table 6, relative reactivity does not change significantly with an increase in the reaction temperature, while relative adsorption constants follow the Arrhenius-type law, previously described (*15*)

$$R \ln K_{D,T} = \Delta S^{ads}_{D,T} - \Delta H^{ads}_{D,T} T^{-1}, \quad (4)$$

where $R$ is the gas constant and $\Delta S^{ads}_{D,T}$ and $\Delta H^{ads}_{D,T}$ are the differential entropy and heat (or enthalpy) of adsorption, respectively, between a triple and a double bond, in each propargyl/allyl pair on the nickel surface. Table 8 collects values of $\Delta S^{ads}_{D,T}$ and $\Delta H^{ads}_{D,T}$ for the three pairs of alcohols. From these values and according to Eq. (4), we can obtain the relative influence of steric and electronic effects (associated with $\Delta S^{ads}/R$ and $-\Delta H^{ads}_{D,T}/RT$, respectively) in the relative adsorption constant $K_{D,T}$. Thus, the relative influence of steric and electronic effects is determined by the operating temperature. The corresponding values of $\Delta H^{ads}_{D,T}/RT$ for an intermediate $T$ = 313 K value and those for $\Delta S^{ads}_{D,T}/R$ are also presented in Table 8.

TABLE 5

Temperature Effects on Areal Rates, $r_A$, obtained for Different Propargyl and Allyl Alcohols with Ni/AlPO$_4$-P under Standard Conditions at 0.41 MPa of Initial Hydrogen Pressure

| Alcohols | $T$ (K) | $r_A \times 10^6$ (mol s$^{-1}$ m$_{Ni}^{-2}$) |
|---|---|---|
| HC≡C—CH$_2$OH | 293 | 0.094 |
| | 303 | 0.153 |
| | 313 | 0.248 |
| | 323 | 0.372 |
| HC≡C—CH(CH$_3$)OH | 293 | 0.465 |
| | 303 | 0.938 |
| | 313 | 1.897 |
| | 323 | 3.250 |
| HC≡C—C(CH$_3$)$_2$OH | 293 | 2.089 |
| | 303 | 4.498 |
| | 313 | 8.053 |
| | 323 | 17.067 |
| H$_2$C═CH—CH$_2$OH | 293 | 20.706 |
| | 303 | 29.871 |
| | 313 | 40.738 |
| | 323 | 54.705 |
| H$_2$C═CH—CH(CH$_3$)OH | 293 | 6.756 |
| | 303 | 10.850 |
| | 313 | 19.729 |
| | 323 | 27.883 |
| H$_2$C═CH—C(CH$_3$)$_2$OH | 293 | 6.823 |
| | 303 | 10.698 |
| | 313 | 15.770 |
| | 323 | 24.800 |

These results indicate that in all cases the very low $K_{D,T}$ values are due to the influences of the electronic contribution through the favorable differential adsorption heat between triple and double bond (negative values for $-\Delta H^{ads}_{D,T}/RT$). Furthermore, this difference increased due to the effects of methyl substitution. The steric effects manifested through differential adsorption

TABLE 6

Temperature Influence on Relative Reactivities, $R_{D,T}$, and on Relative Adsorption Constants, $K_{D,T}$, in the Consecutive Hydrogenation of Different Propargyl Alcohols with Ni/AlPO$_4$-P.

| T (K) | P-en/P-yn | | B-en/B-yn | | MB-en/MB-yn | |
|---|---|---|---|---|---|---|
| | $R_{D,T}$ | $K_{D,T} \times 10^3$ | $R_{D,T}$ | $K_{D,T} \times 10^3$ | $R_{D,T}$ | $K_{D,T} \times 10^3$ |
| 293 | 0.151 | 0.688 | 0.241 | 16.59 | 0.172 | 52.66 |
| 303 | 0.153 | 0.785 | 0.248 | 21.45 | 0.175 | 73.58 |
| 313 | 0.151 | 0.918 | 0.248 | 23.84 | 0.181 | 92.43 |
| 323 | 0.160 | 1.089 | 0.243 | 28.32 | 0.181 | 124.56 |

entropy are also closely related to methyl substitution effects. Thus, in the pair P-yn/P-en, negative values for $\Delta S^{ads}_{D,T}/RT$ promote an additional decrease in $K_{D,T}$ value while those that are positive for the B-yn/B-en and MB-yn/MB-en pairs do the opposite. Consequently, the adsorption of a triple bond is hindered to a greater degree than that of a double one through methyl substitution.

On the other hand, the values of $\Delta E_a$ and $\Delta H^{ads}_{D,T}$ for each reactant pair coincide within experimental error, as can be seen in Table 8 where $\Delta E_a$ values are also included. Similar behavior was previously obtained in the competitive hydrogenation of allyl alcohols on supported nickel catalysts (*15*) and it is related to the independence of $R_{D,T}$ with respect to the reaction temperature. Thus, according to Chihara and Tanaka (*52*), the temperature dependence of relative reactivity, $R_{D,T}$, is given by the difference between the true activation energies of the two substrates according to the Arrhenius-type law

$$R\frac{d(\ln R_{A,B})}{d(1/T)} = -(E_{a_A} + \Delta H_A{}^{ads}) + (E_{a_B} + \Delta H_B{}^{ads}) = -\Delta E_{true\ A,B}) \qquad (5)$$

where the quantity $(E_a + \Delta H^{ads})$ is the true activation energy, $E_{true}$, representing the energy required for bringing the adsorbed substrate to the activated state (negative values for exothermic). When we consider another formulation of this expression,

$$R\frac{d(\ln R_{A,B})}{d(1/T)} = -(E_{a_A} - E_{a_B}) - (\Delta H_A^{ads} - \Delta H_B^{ads}), \qquad (6)$$

we see that the absence of change in $R_{D,T}$ in the range of temperatures studied may be ascribed to the relation

TABLE 7

Activation Parameters and their Respective Standard Deviations Obtained for Different Unsaturated Alcohols with Ni/AlPO$_4$-P: Apparent Activation Energies, $E_a$, Arrhenius Constant, ln *A*, Activation Enthalpies, $\Delta H^{\neq}$, and Activation Entropies, $\Delta S^{\neq}$

| Alcohols | $E_a$ (kJ mol$^{-1}$) | ln *A* | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|
| $HC{\equiv}C{-}CH_2OH$ | 36.3 ± 0.5 | −1.3 ± 0.2 | 33.8 ± 0.5 | −265 ± 2 |
| $HC{\equiv}C{-}CH(CH_3)OH$ | 51.5 ± 1.0 | 6.6 ± 0.5 | 49.0 ± 1.0 | −200 ± 5 |
| $HC{\equiv}C{-}C(CH_3)_2OH$ | 54.0 ± 2.0 | 9.2 ± 0.8 | 51.6 ± 2.0 | −178 ± 7 |
| $H_2C{=}CH{-}CH_2OH$ | 25.4 ± 0.4 | −0.3 ± 0.2 | 22.9 ± 0.5 | −257 ± 1 |
| $H_2C{=}CH{-}CH(CH_3)OH$ | 38.0 ± 2.0 | 3.8 ± 0.9 | 35.7 ± 2.0 | −223 ± 7 |
| $H_2C{=}CH{-}C(CH_3)_2OH$ | 33.5 ± 1.0 | 1.9 ± 0.4 | 31.0 ± 1.0 | −239 ± 3 |

TABLE 8

Experimental Values for $\Delta H^{\mathrm{ads}}_{\mathrm{D,T}}$ and $\Delta E_{\mathrm{a}}{}^{a}$, $\Delta D^{\mathrm{ads}}_{\mathrm{D,T}}{}^{b}$, and the Corresponding Values of $\Delta S^{\mathrm{ads}}_{\mathrm{D,T}}/R$ and $\Delta H^{\mathrm{ads}}_{\mathrm{D,T}}/RT$ ($T = 313$ K) for Ni/AlPO$_4$-P Catalyst in Different Pairs of Competing Reactants in a Consecutive Process

| | P-en/P-yn | B-en/B-yn | MB-en/MB-yn |
|---|---|---|---|
| $\Delta H^{\mathrm{ads}}_{\mathrm{D,T}}$ | 12.0 ± 0.7 | 13.0 ± 1.0 | 21.9 ± 0.9 |
| $\Delta S^{\mathrm{ads}}_{\mathrm{D,T}}$ | −19.0 ± 2.0 | 12.0 ± 5.0 | 51.0 ± 3.0 |
| $-(E_{\mathrm{aD}} - E_{\mathrm{aT}})$ | 10.9 | 13.5 | 20.5 |
| $\Delta S^{\mathrm{ads}}_{\mathrm{D,T}}/R$ | −2.3 | 1.5 | 6.2 |
| $\Delta H^{\mathrm{ads}}_{\mathrm{D,T}}/RT$ | −4.6 | −5.0 | −8.5 |

[a] In kJ mol$^{-1}$.

[b] In J mol$^{-1}$ K$^{-1}$.

$$\Delta H^{\mathrm{ads}}_{\mathrm{D,T}} \simeq -\Delta E_{\mathrm{a}_{\mathrm{D,T}}} \tag{7}$$

shown in Table 8. In this respect, from Eq. (5) we also see identical values for the true activation energies in the liquid-phase catalytic hydrogenation of the double and triple bonds, $E_{\mathrm{true,T}} \simeq E_{\mathrm{true,D}}$.

Accordingly, the action of an additional C–C bond in an olefinic double bond (to give an alkyne one) on its catalytic hydrogenation mechanism is similar to that of another substituent such as a methyl group. This conclusion is also supported by the identical $E_{\mathrm{true}}$ values for allyl alcohol and its methyl derivatives obtained from their competitive hydrogenation under the present experimental conditions (*15*). This independence of $E_{\mathrm{true}}$ from substituents as well as the existence of a Polanyi relationship (*53, 54*) associated with Eq. (7) was ascribed, according to Boudart (*53*), to the existence of a linear free-energy relationship (LFER) which manifested itself in a linear relation between the entropy and enthalpy,

$$\Delta G^{\neq}_{\mathrm{const}} = -\theta R \ln K^{\neq} = \Delta H^{\neq} - \theta \Delta S^{\neq}, \tag{8}$$

known as the "compensation effect" or the "isokinetic relationship" (IKR) (*55, 56*) although the most habitual representation is through the equation

$$\ln A = \ln \alpha + E_{\mathrm{a}}/\theta R, \tag{9}$$

where $\theta$ is the "isokinetic temperature" at which identical values of the reaction rate $r_{\mathrm{A}} = \alpha$ are obtained. $\theta$ temperature is also considered to be the vibrational temperature of the reaction center (or core) of the active adsorption complex (*57*). $K^{\neq}$ is the equilibrium constant of the activated complex and $\Delta G^{\neq}$ its activation free energy.

From activation parameters ($E_{\mathrm{a}}$, ln $A$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$) collected in Table 7, a series of common isokinetic parameters (Table 9) is obtained from slopes and intercepts in Eqs. (8) and (9). This is done by plotting $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ and ln $A$ vs $E_{\mathrm{a}}$, as shown in Fig. 3 for the former, where a linear plot with the regression coefficient, $r$, over 0.9 is obtained with all substrates. However, better correlations may be obtained ($r \simeq 0.99$) by separately plotting both kinds of substrates, olefins, and alkynes. As can be seen in Table 9, where the corresponding isokinetic parameters for both sets of unsaturated alcohols are also present, the corresponding free energy values for olefins and alkynes, $\Delta G^{\neq}_{\mathrm{D}}$ and $\Delta G^{\neq}_{\mathrm{T}}$, respectively, are not identical although they are similar enough to exhibit a common LFER between double and triple bonds, allowing us to obtain identical $E_{\mathrm{true}}$ values from the kinetic study of the consecutive hydrogenation reactions.

In this respect, if a compensation effect holds for a reaction series exhibiting a similar $\Delta G^{\neq}$ value, a common transition state intermediate can be expected (*58–60*). The similar $\Delta G^{\neq}$ values collected in Table 9 indicate that a similar common interaction mechanism should be considered in the liquid-phase catalytic hydrogenation of methyl-substituted allyl and propargyl alcohols in spite of the possible difference detected in Fig. 3. Here we can see that in the activation process (as well as in the adsorption process), methyl substitution operates by lessening the relative contribution of steric effects (through $\Delta S^{\neq}/R$) with respect to electronic effects (through $\Delta H^{\neq}/RT$) to the free-energy of the transition state over the experimental temperature range.

TABLE 9

Values of $\ln \alpha$ and $\theta^a$ ($K$) Obtained from the Representation of $\ln A$ vs $E_a$ and Values of $\theta^b$ ($K$), $\Delta G^{\neq}$ (kJ $mol^{-1}$), and $\ln K^{\neq}$ Obtained from the Representation of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$, Corresponding to Substrates with Ni/$AlPO_4$-P Catalyst

| Substrates | $\ln \alpha$ | $\theta^a$ | $\theta^b$ | $\Delta G^{\neq}$ | $\ln K^{\neq}$ |
|---|---|---|---|---|---|
| Allyl alcohols | $-9 \pm 1$ | $381 \pm 44$ | $375 \pm 43$ | $121 \pm 10$ | $-39 \pm 6$ |
| Propargyl alcohols | $-22 \pm 3$ | $212 \pm 22$ | $212 \pm 22$ | $91 \pm 5$ | $-52 \pm 6$ |
| All together | $-10 \pm 3$ | $365 \pm 92$ | $293 \pm 73$ | $104 \pm 17$ | $-43 \pm 13$ |

fects (through $\Delta S^{\neq}/R$) with respect to electronic effects (through $\Delta H^{\neq}/RT$) to the free-energy of the transition state over the experimental temperature range.

On the other hand, the same *cis*-concerted mechanism, previously described (*34*) in the liquid-phase hydrogenation of methyl-substituted allyl alcohols on Rh/$AlPO_4$ catalysts as well as in the liquid-phase catalytic hydrogenation of several styrene derivatives on supported nickel catalysts (*61*), may explain not only the hydrogenation reaction of allyl alcohols on Ni/$AlPO_4$-P but also those of propargyl alcohols. This possibility arises from the actual kinetic parameters obtained in the individual as well as in the consecutive processes. Thus, the relatively low values of $\Delta S^{\neq}$ (negative) for all unsaturated alcohols (Table 7) indicate that, on going from the ground state to the transition state, an extensive restriction in degrees of freedom must be considered. Likewise, the existence of common kinetic behavior (zero order with respect to hydrogen pressure and substrate concentration) of common isokinetic parameters as well as of a common $E_{true}$ for every pair of allyl/propargyl alcohols prompts us to consider a concerted evolution for a highly ordered common transition state.

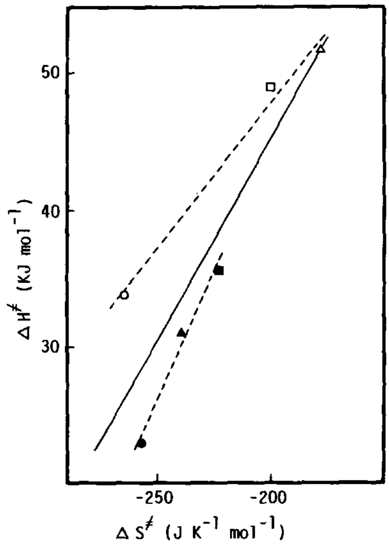

FIG. 3. Compensation effect between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values in Table 6 for different unsaturated alcohols: (○) 2-propyn-1-ol, (□) 3-butyn-2-ol, (△) 2-methyl-3-butyn-2-ol, (●) 2-propen-1-ol, (■) 3-buten-2-ol, and (▲) 2-methyl-3-buten-2-ol.

In the present mechanism the active sites on the nickel surface are regarded as surface complexes (*62–64*) with three degrees of coordinative unsaturation where it is possible to adsorb two hydrogens and an olefin (or alkyne) at the same time. The transfer of the two hydrogens to the unsaturated bond through a concerted process leads directly to alkane (or alkene) formation. Moreover, this kind of active site, where the simultaneous and noncompetitive adsorption of hydrogen and olefin (or alkyne) occurs, can explain the zero-order kinetics with respect to hydrogen pressure and olefin concentration because, in the range of operating variables, the active sites are all (simultaneously) covered with both reactant molecules.

On the other hand, methyl substitution, as well as the effects of a support and/or a second metal on the catalytic activity (explained as a donor–acceptor interaction between the frontier orbitals of catalysts and substrates), may be better understood in the context of such a concerted mechanism, according to the terminology proposed by Dewar and co-workers (*65, 66*).

## CONCLUSIONS

On the basis of these results, we may conclude that the modification introduced into the classical Rader–Smith relation (*41*) in Eq. (3) allows us to obtain $R_{D,T}$ and $K_{D,T}$ values in consecutive processes such as the selective hydrogenation of alkynes within the framework of Langmuir–Hinshelwood kinetics, so that they can be used in the same way as those obtained in competitive reactions.

By using this information, we obtain valuable information not only concerning the mechanism of the liquid-phase hydrogenation of propargyl alcohols on Ni–$AlPO_4$ catalysts but also on the parameters affecting the selectivity of the process: the electronic density of double and triple bonds, increased by the effects of methyl substitution as well as the electronic level of supported nickel, which is modified by metal–support interaction effects or by Ni–Cu alloying. An increase in electronic density in these parameters promotes a variable increase in the $K_{D,T}$ joined to a variable decrease in $r_D/r_T$. Taking into account that $R_{D,T}$ is obtained as the product of the two parameters, an especially high degree of selectivity could be obtained by the appropriate blend of support, metal, and promoter.

According to these results, Ni–Cu alloys seem to be a good candidate, not only due to their high degree of selectivity toward allyl alcohols, which may be enhanced by a more adequate proportion between the two metals, but also because there was no formation of the corresponding carbonyl compound through isomerization of the double bond as was obtained with Rh/$AlPO_4$ (*34*) and also described for Rh and Pd blacks (*9*).

In spite of the loss of the normal chemisorption capacity associated with SMSI effects, the Ni/$AlPO_4$ catalysts are useful as catalysts for the hydrogenation of alkenes because they present greater activity, per unit weight of nickel, than those of the Ni/$SiO_2$ or Ni/$Al_2O_3$ catalysts in the liquid-phase hydrogenation of 1-hexene (*10*). This fact was related to the higher saturation ability of the $AlPO_4$ support for Ni metal than for conventional supports like $Al_2O_3$ or $SiO_2$ (*11*). Therefore, the $AlPO_4$ could be an adequate support component to enable a tailored Ni–Cu catalyst to obtain the most appropriate activity and selectivity in the consecutive semihydrogenation of propargyl alcohols, and more exactly to obtain selectively 2-methyl-3-buten-2-ol, a key step in the production of isoprene through a dehydration reaction (*5*). Further work on this research is in progress.

## ACKNOWLEDGMENTS

This work was subsidized by a grant for scientific research from the Comisión de Investigación Científica y Técnica (CICYT, Project PA86-0065), Ministerio de Educación y Ciencia. Furthermore, financial aid from the Consejería de Educación y Ciencia de la Junta de Andalucía, Spain, is gratefully acknowledged. The authors also acknowledge the grammatical revision of the manuscript carried out by Professor M. Sullivan and the valuable help of Professor C. Jiménez in the hydrogen chemisorption experiments.

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