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$AlPO_4$-Supported Nickel Catalysts

VI. Support Effects on the Individual and Competitive Hydrogenation of Allyl Alcohol and Its α and β Methyl Derivatives

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Individual and competitive liquid-phase hydrogenation of allyl alcohols (2-propen-1-ol, 2-methyl-2-propen-1-ol, and 2-buten-1-ol) has been carried out at 293–313 K and 0.41 MPa of initial hydrogen pressure on nickel catalysts at 20 wt% supported on Al_2O_3, SiO_2, and on three different types of $AlPO_4$. Furthermore, unsupported bulk nickel was employed as catalyst. The independence of the relative reactivities, R, with respect to the temperature and the Arrhenius-type law obtained for the relative adsorption constants, K, from ln K vs T^{-1}, in all studied catalysts, was associated with the existence of a linear free-energy relationship (LFER) which also manifested itself in a linear relationship between the differential adsorption heat, $\Delta\omega$, and differential entropy factors, ΔS. According to the values of both kinds of parameters ($\Delta\omega$ and ΔS) for every catalyst, it was concluded that the steric effects on the CH_3 adsorption decreased in the order Ni/$AlPO_4$-P > Ni/$AlPO_4$-F > Ni/SiO_2 > Ni/Al_2O_3 > Ni/$AlPO_4$-B > Ni bulk; which is exactly the opposite of the inductive effect. -P, -F, and -B refer to the precipitation agent employed in the synthesis of $AlPO_4$: propylene oxide, ammonia, and ethylene oxide, respectively. Such LFER also manifested itself in the existence of a linear correlation between log A and E_a (Arrhenius constant and apparent activation energy, respectively) known as "compensation effect." The existence of this LFER is adscribed to the independence of the true activation energy from substituent and catalyst effects in these hydrogenation processes.

INTRODUCTION

The applicability of aluminum phosphates and some binary and ternary mixed systems such as nickel supports have been the subject of several studies and patents in recent years (*1–14*). These reports have shown the utility of $AlPO_4$-supported nickel catalysts in the liquid-phase hydrogenation of the carbon–carbon double bond of several compounds. Besides, the existence of metal–support interactions on these systems has been supported on the kinetic behavior of the catalysts (*5–11*), on the suppression of hydrogen chemisorption (*12*), and, lastly, with the help of a poisoning titration method (*15*).

Recently, we have studied methyl substitution effects by means of the competitive hydrogenation of styrene and its α-methyl derivative over $AlPO_4$-supported Ni (*10*) and Rh (*16, 17*) catalysts. From results obtained in these studies and those published by Cerveny *et al.* (*18–20*), we considered the possibility of studying the support effects from the kinetic data obtained in the individual and competitive hydrogenation of selected pairs under specified conditions.

The present paper reports on an investigation into the individual and competitive hydrogenation of allyl alcohol (A, 2-propen-1-ol) and its two methyl derivatives, methallyl alcohol (M, 2-methyl-2-propen-1-ol) and crotyl alcohol (C,2-buten-1-ol). Reactions are carried out in methanol as the solvent, at low initial hydrogen pressure (0.4–0.6 MPa), and temperatures between 293 and 313 K, over a series of nickel catalysts at 20 wt% supported on Al_2O_3, SiO_2, and three different types of $AlPO_4$ synthesized according to Kearby (*21*), employing three different precipitation agents, ammo-

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nia, ethylene oxide, and propylene oxide. Unsupported nickel metal has also been employed as a catalyst.

EXPERIMENTAL

Supports

Five different supports have been used: commercial silica (SiO_2) from Merck (Kieselgel 60, 230 mesh), a commercial alumina (Al_2O_3) (aluminum oxide active, acidic for chromatography) from Merck, and three aluminum orthophosphates prepared according to Kearby (*21*) by precipitation from aluminum chloride and phosphoric acid (aqueous solutions), using ammonium hydroxide solution ($AlPO_4$-F), ethylene oxide ($AlPO_4$-B), and propylene oxide ($AlPO_4$-P), respectively. The pH value at the precipitation "endpoint" was in all cases 6.1. The solids obtained were washed with isopropanol and dried at 393 K for 24 h. In all cases, the composition was $Al/P = 1$.

The resulting powders screened to <0.149 mm were calcined at 920 K for 3 h. Both commercial supports, Al_2O_3 and SiO_2, were subjected to the same calcination treatment. The detailed synthesis procedure and textural properties (surface area, pore volume, and main pore diameter, determined by nitrogen adsorption, BET method) have been published elsewhere (*22–24*) and are summarized in Table 1.

TABLE 1

Textural Properties of the Supports

Support	S^a	V^b	d_v^c
SiO_2	380	0.40	2.0
Al_2O_3	73	0.31	2.0
$AlPO_4$-F	181	0.40	3.6
$AlPO_4$-B	256	0.60	4.5
$AlPO_4$-P	210	0.42	2.5

[a] Surface area, $m^2\ g^{-1}$.

[b] Pore volume, $ml\ g^{-1}$.

[c] Main pore diameter, nm.

Catalysts

Catalysts containing 20 wt% nickel were prepared by impregnation of the supports to incipient wetness with 10 *M* aqueous solutions of nickel nitrate. They were dried, crushed, and screened to a particle size <0.149 mm (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 and stored in sealed glass bottles until required. A more detailed description of the synthesis procedure has been reported previously (*7, 11*). Bulk nickel was obtained by reduction of nickel oxide (Merck, p.a.) under the same conditions employed with the supported nickel systems.

Dispersion Measurements

Metal surface areas, S, of different catalysts were determined from the average crystallite diameter D, obtained by X-ray diffraction technique (XRD) according to the method of Moss (*25*) as reported in previous papers (*7–11, 15, 26*). X-Ray line broadening experiments were conducted with a Philips Model 1103/00/60 diffractometer, using Co$K\alpha$ radiation. A scan speed of 7.5° h^{-1} was used for the 2θ range between 46 and 56° for the determination of the width of the (111) nickel peak at half height.

The metal surface area of bulk Ni had been previously obtained (*15*) using XRD and transmission electron microscopy (TEM). The values obtained by both techniques were in very close agreement: $S_{XRD} = 13.1$ and $S_{TEM} = 15.0\ m^2 g_{Ni}^{-1}$, respectively.

Catalytic Activity

According to the procedure described previously (*5–11*), individual and competitive hydrogenation runs were carried out under vigorous shaking in a conventional low-pressure hydrogenator (Parr Instrument Co., Md. 3911) equipped with a manometer which constantly monitored the hydrogen pressure in the isolated reaction vessel (500 ml). The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket, with an accuracy of ±0.5 K.

Allyl, methallyl, and crotyl alcohols were obtained from Merck p.a. and purified by distillation under reduced pressure and low temperature and then passed through active acidic aluminum oxide powder for chromatography (Merck) activated at 673 K in flowing ultrapure nitrogen. Hydrogen (99.999%, SEO) and methanol (p.a. 99%, Panreac) were used without further purification.

Individual reactions were carried out under essentially constant-volume conditions, in 25 ml of 1 *M* methanolic solution of substrate, under an initial hydrogen pressure of 0.41 MPa and temperatures in the range 298–313 K. All throughout, 0.15 g of catalyst was employed, except with the nickel bulk, where 0.5 g was used.

The initial reaction rates, for individual hydrogenation, were obtained from the hydrogen uptake (calculated from the lowering of the hydrogen pressure at the manometer) as a function of time. As plots of the decrease of the hydrogen pressure with time were always linear up to 80–90% conversion, the determination of the initial slope 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 catalyst.

For competitive hydrogenation, 25 ml of equimolecular mixtures of allyl/methallyl, allyl/crotyl, or methallyl/crotyl alcohols in methanol (0.5×10^{-3} mol of each) were hydrogenated under experimental conditions identical to the individual hydrogenations. The reactions were followed by GLC analyzing the reaction mixtures at appropriate intervals of hydrogen uptake. GLC analysis were performed with a Hewlett–Packard 5830 gas chromatograph fitted with a H.P. 18850 GC terminal, equipped with a column packed with 5% polyphenylether in 80/100 Chromosorb GAW-DMCS. The only products detected were the corresponding unsaturated or saturated alcohols. Neither isomerization nor hydrogenolysis products were detected in any of the cases.

RESULTS AND DISCUSSION

Individual Hydrogenation

The hydrogen diffusion control in the reactions was examined. 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 above 200 strokes min^{-1}. The internal diffusion was excluded by using catalysts with a grain diameter <0.149 m. As may be seen in Table 2, where the hydrogenation rates of allyl alcohol are collected under standard conditions, on 20 wt% Ni/AlPO$_4$-P catalysts of several grain sizes, the internal diffusion control operates when the grain size is greater than 0.21 mm.

Furthermore, a linear variation between the weight of the catalyst, w, and the hydrogen uptake rate, r, was obtained. The plot of r^{-1} vs w^{-1} was also linear, and from the inverse of the interception at origin (*27*), a hydrogen transfer rate of 0.29×10^{-3} mol s^{-1} was obtained. Due to the fact that the whole reaction exhibits a hydrogen uptake rate 10–12 orders of magnitude lower than this limit, we have to conclude that in the

TABLE 2

Influence of the Grain Diameter, $\bar{d}$, of Ni/AlPO$_4$-P Catalyst on the Areal Rate, r_A, in the Liquid-Phase Catalytic Hydrogenation of Allyl Alcohol under Standard Conditions ($T = 293$ K, $P_{H_2} =$ 0.41 MPa)

$\bar{d}$ (mm)	$r_A \times 10^6$ (mol s^{-1} g_{Ni})
$\bar{d} < 0.074$	32.5
$0.074 < \bar{d} < 0.149$	33.3
$0.149 < \bar{d} < 0.210$	28.6
$0.210 < \bar{d}$	11.5

range of operating variables, the kinetic data are free from transport influences.

The hydrogenation rates for all three substrates, allyl, methallyl, and crotyl alcohols, were zero order in the substrate concentration (0.5–3 *M*) as well as in hydrogen pressure (0.35–0.50 MPa). This behavior is the same as those previously found (*5–9*) in the liquid-phase catalytic hydrogenation of the olefinic double bond of several substrates on $Ni/AlPO_4$ catalysts. Clearly, the same mechanism can be applied to all cases. Thus, it may be described within the framework of the Langmuir–Hinshelwood kinetic models, by a classical Horiuti–Polyani type mechanism, noncompetitive (*28*), with interconversion between monoadsorbed and diadsorbed species and with the formation of a π allylic species that is delocalized on three carbon atoms.

According to the results summarized in Table 3, where the specific areal rates, r_A,

TABLE 3

Areal Rates, r_A, of Different Catalysts in the Individual Hydrogenation of Allyl (A), Methallyl (M), and Crotyl (C) Alcohols under 0.41 MPa of Initial Hydrogen Pressure

Catalyst	D^a (nm)	S^b ($m^2\ g_{Ni}^{-1}$)	T^c (K)	$r_A \times 10^6$ ($mol\ s^{-1}\ m_{Ni}^{-2}$)		
				A	M	C
Ni bulk	59.7	13.1	293	3.64	0.98	2.00
			298	6.61	1.20	2.38
			303	11.36	1.53	2.96
			308	12.98	1.90	3.55
			313	14.99	2.20	4.29
Ni/SiO_2	15.1	44.5	293	15.64	8.80	9.82
			298	21.97	11.51	12.87
			303	25.38	13.79	17.99
			308	34.97	16.80	22.91
			313	40.15	23.01	25.79
Ni/Al_2O_3	25.2	26.8	293	11.22	5.98	8.29
			298	14.13	6.89	9.15
			303	17.39	8.09	10.36
			308	22.33	9.62	12.27
			313	27.42	10.93	13.42
$Ni/AlPO_4$-F	11.9	55.6	293	22.92	4.67	4.86
			298	28.75	6.70	6.59
			303	36.29	7.63	8.91
			308	45.28	11.56	10.53
			313	47.62	13.63	14.77
$Ni/AlPO_4$-B	6.8	98.7	293	4.80	3.17	2.14
			298	7.94	3.59	2.48
			303	8.91	4.19	2.96
			308	11.64	5.34	3.52
			313	15.13	6.35	4.28
$Ni/AlPO_4$-P	20.9	32.2	293	24.76	6.31	6.82
			298	33.30	7.77	11.41
			303	36.68	12.24	14.51
			308	41.64	15.30	18.23
			313	48.65	18.17	22.95

[a] Average crystallite diameter.

[b] Metal surface area per gram of supported nickel.

[c] Reaction temperature.

of nickel catalysts at different temperatures are reported, we can conclude that all the supports enhance the catalytic activity of nickel to a variable degree. This behavior was previously obtained (*15*) in 1-hexene hydrogenation with Ni/$AlPO_4$-B, Ni/$AlPO_4$–SiO_2, Ni/SiO_2, and Ni bulk catalysts and studied with the help of a poisoning titration method. Such behavior was associated with a strong metal–support interaction which may be explained by electronic effects.

From r_A values in the hydrogenation of allyl alcohol we find that the enhancement of Ni due to effects of the support decreases in the sequence Ni/$AlPO_4$-P $\geq$ Ni/$AlPO_4$-F $\geq$ Ni/SiO_2 $>$ Ni/Al_2O_3 $>$ Ni/$AlPO_4$-B $>$ Ni bulk, while for methyl derivatives of allyl alcohol the sequence obtained is Ni/SiO_2 $\geq$ Ni/$AlPO_4$-P $\geq$ Ni/$AlPO_4$-F $>$ Ni/Al_2O_3 $>$ Ni/$AlPO_4$-B $>$ Ni bulk.

This relatively good agreement could be easily explained taking into account the support influence in the methyl substituent effects since the areal rate of a Ni/support catalyst is not only determined by the activity of the nickel, which depends on the electron density on nickel, but is also affected by the steric hindrance of the reactant molecules. Thus, the methyl steric effect is lower in Ni/SiO_2 than in the other Ni/support catalysts.

However, if we consider in Table 4 the values of apparent activation energy, E_a, and the preexponential factor, log A, obtained from the Arrhenius expression by plotting log r_A vs T^{-1} values in Table 3, some fundamental questions arise. Thus, E_a values for allyl alcohol closely fit the sequence obtained for r_A values, while E_a for M and C (α and β methyl derivatives of allyl alcohol) not only do not fit this sequence, as ought to be expected, but also do not even fit their own. Furthermore, on going from allyl alcohol to its methyl derivatives, M or C, we obtain a notable decreasing in E_a in some catalysts (Ni bulk, Ni/Al_2O_3, and Ni/$AlPO_4$-B). In other catalysts (Ni/$AlPO_4$-P and Ni/$AlPO_4$-F) there is an increase and, finally, in Ni/SiO_2 the change is negligible.

Accordingly, we have to conclude the impossibility of extending the results obtained in the individual hdyrogenation of the olefinic double bond of a substrate with a series of catalysts to other substrates because, due to the effect of the simplest substitution (a $-CH_3$ by H), we have dramatic changes in E_a, log A, and consequently in the catalytic activity.

At this point it is interesting to note that, in all cases, E_a, log A, and r_A for M and C practically coincide for all catalysts studied so that it is easy to conclude that the effects of methyl substitution in α or β are very similar.

TABLE 4

Apparent Activation Energies (E_a, kJ mol^{-1}) and Arrhenius Constants (log A, mol s^{-1} m_{Ni}^{-1}) for all Catalysts and Substrates Studied[a]

Catalyst	Allyl alcohol		Methallyl alcohol		Crotyl alcohol	
	E_a	log A	E_a	log A	E_a	log A
Ni bulk	53.86 ± 9.99	4.27 ± 1.74	30.80 ± 1.24	−0.50 ± 0.30	30.11 ± 0.60	−0.32 ± 0.07
Ni/SiO_2	35.78 ± 2.94	1.60 ± 0.50	34.89 ± 2.29	1.19 ± 0.39	38.13 ± 3.18	1.83 ± 0.55
Ni/Al_2O_3	34.57 ± 0.72	1.23 ± 0.13	23.37 ± 0.66	−1.04 ± 0.11	19.04 ± 1.20	−1.67 ± 0.20
Ni/$AlPO_4$-F	29.16 ± 3.03	0.59 ± 0.51	40.80 ± 3.77	1.98 ± 0.65	40.84 ± 2.18	2.00 ± 0.38
Ni/$AlPO_4$-B	40.70 ± 4.82	2.00 ± 0.82	27.09 ± 2.16	−0.66 ± 0.37	26.27 ± 1.06	−0.97 ± 0.18
Ni/$AlPO_4$-P	24.40 ± 2.82	−0.22 ± 0.37	42.44 ± 4.00	2.39 ± 0.68	44.09 ± 4.85	2.77 ± 0.83

[a] Uncertainties are determined for a 95% confidence limit.

Competitive Hydrogenation

According to the classical theory of competitive hydrogenation (*29, 30*) and assuming that the reaction rate of each olefin is first order in the amount adsorbed and also that the adsorption of both olefins follow the Langmuir isotherm, the kinetics of a competitive hydrogenation of A and M alcohols can be expressed by the equation

$$R_{M,A} = \frac{r_M}{r_A} K_{M,A} = \log \frac{C^0_M}{C_M} \Big/ \log \frac{C^0_A}{C_A}, \quad (1)$$

where $R_{M,A}$ is the relative reactivity and represents an index of the reactivity of M compared to that of A; r_M and r_A are, respectively, the individual initial rates of M and A; and $K_{M,A}$ is the relative adsorption constant of M to A which may be used as a measure of the relative strength of adsorption; C_A, C_M, C^0_A, and C^0_M represent the actual and initial concentrations of A and M, respectively.

The competitive hydrogenation of equimolecular mixtures of A/M, A/C, and M/C gave the two different reactions patterns shown in Fig. 1, with the different catalysts studied. Thus, the selectivity of A vs M and C was very high while M vs C was very close to unity. Relative reactivities, *R*, were calculated from the slopes of the straight lines obtained in their log–log plots according to Eq. (1). The linearity of these plots can be taken as evidence of the validity of the applied theoretical treatment. The results obtained are collected in Table 5, where *K* values are also represented. The values of *K* were obtained, according to Eq. (1), from *R* and the corresponding individual hydrogenation rates.

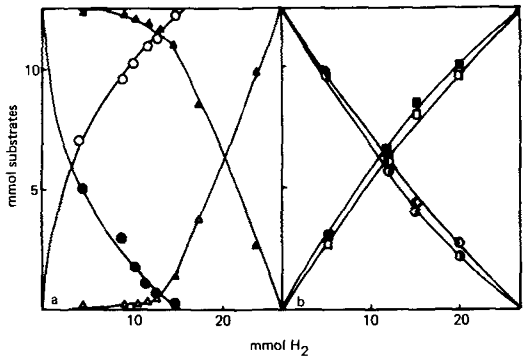

FIG. 1. Differential pattern in the competitive hydrogenation of A/M and A/C (a) respect to M/C (b) on Ni/$AlPO_4$-P at standard experimental conditions. (a) Allyl alcohol (●); propanol (○); methallyl or crotyl alcohol (▲); and isobutyl alcohol or *n*-butanol (△), respectively. (b) Methallyl alcohol (◐); isobutyl alcohol (□); crotyl alcohol (◑); and *n*-butanol (■).

It is also interesting to note that *R* values in Table 5, for all catalysts and temperatures, fulfill, within the experimental error, the expression

$$R_{M,A}/R_{C,A} = R_{M,C}. \quad (2)$$

According to Cerveny *et al.* (*19*) the relation would not be satisfied, if specific interactions occurred between the individual substrates. The results obtained so far indicate that such specific interactions are not so important as to invalidate (2) so that Eq. (1) was suitably employed. In connection with this Boudart and Djega-Moriadassou (*31*) consider that this pattern remains one of the most convincing arguments in favor of the self-consistency of kinetic parameters based on the theory of uniform surfaces.

According to the low values of $R_{M,A}$ and $R_{C,A}$ the hydrogenation of allyl alcohol vs its methyl derivatives is very selective $\simeq$ 70–85%. This is due to the low values of $K_{M,A}$ and $R_{C,A}$ and also to the low values of r_M/r_A and r_C/r_A. In the present case the methyl substitution effects reduce both individual rates and the relative adsorption constant so that the obtained selectivity is higher than in the styrene/α-methylstyrene pair (*10*) with the catalysts Ni/$AlPO_4$-B, Ni/$AlPO_4$–Al_2O_3, and Ni/$AlPO_4$–SiO_2, where the obtained relative adsorption constants $K_{M,S}$ were very similar to $K_{M,A}$ and $K_{C,A}$ but the individual hydrogenation rates, r_{MS} and r_S, were very similar for both substrates.

Besides, there is a clear influence of the support in the selectivity of the allyl alcohol vs its methyl derivative, as illustrated in Fig. 2, where "*t*-test" of significance show that correlations between selectivity ($R_{M,A}$

TABLE 5

Relative Reactivities, *R*, and Relative Adsorption Constants, *K*, for the Competitive Hydrogenation of Allyl (A), Methallyl (M), and Crotyl (C) Alcohols on Different Catalysts at Several Temperatures under 0.41 MPa of Initial Hydrogen Pressure

Catalyst	*T* (K)	Allyl/methallyl		Allyl/crotyl		Methallyl/crotyl	
		$R_{M,A}$	$K_{M,A}$	$R_{C,A}$	$K_{C,A}$	$R_{M,C}$	$K_{M,C}$
Ni bulk	293	0.018	0.067	0.016	0.029	1.14	2.32
	298	0.019	0.104	0.016	0.044	1.14	2.26
	303	0.017	0.126	0.015	0.058	1.19	2.30
	308	0.017	0.136	0.015	0.055	1.20	2.24
	313	0.019	0.130	0.016	0.056	1.14	2.22
Ni/SiO_2	293	0.029	0.051	0.030	0.048	0.95	1.06
	298	0.029	0.056	0.028	0.048	0.95	1.06
	303	0.029	0.053	0.030	0.042	0.92	1.20
	308	0.029	0.061	0.029	0.044	0.89	1.20
	313	0.029	0.051	0.028	0.043	0.95	1.06
Ni/Al_2O_3	293	0.015	0.028	0.018	0.024	0.99	1.38
	298	0.015	0.031	0.019	0.029	1.02	1.36
	303	0.015	0.032	0.018	0.030	0.97	1.25
	308	0.015	0.035	0.018	0.033	0.95	1.21
	313	0.015	0.038	0.019	0.038	0.94	1.16
$Ni/AlPO_4$-F	293	0.018	0.088	0.019	0.088	0.92	0.94
	298	0.019	0.081	0.018	0.079	0.95	0.94
	303	0.016	0.076	0.019	0.077	0.91	1.06
	308	0.018	0.070	0.018	0.077	0.93	0.85
	313	0.018	0.063	0.020	0.064	0.89	0.97
$Ni/AlPO_4$-B	293	0.024	0.036	0.025	0.056	0.97	0.66
	298	0.022	0.048	0.024	0.076	0.98	0.68
	303	0.023	0.049	0.024	0.077	0.99	0.68
	308	0.023	0.050	0.025	0.082	1.02	0.67
	313	0.022	0.052	0.025	0.088	0.98	0.66
$Ni/AlPO_4$-P	293	0.023	0.090	0.026	0.094	1.00	1.08
	298	0.021	0.090	0.025	0.072	0.96	1.40
	303	0.021	0.063	0.025	0.063	0.95	1.13
	308	0.022	0.060	0.026	0.059	0.95	1.13
	313	0.022	0.059	0.026	0.055	1.03	1.30

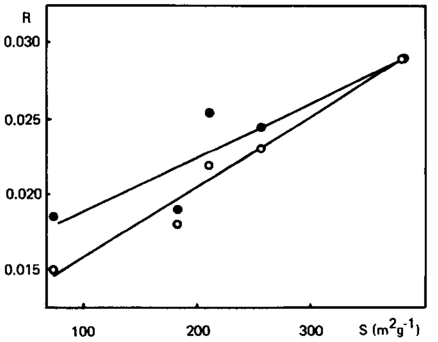

FIG. 2. Influence of support surface area *S* (in Table 1) on relative reactivity *R* (T = 303 K, in Table 5). (O) $R_{M,A}$ and (●) $R_{C,A}$.

and $R_{C,A}$, in Table 5) and support surface area (*S* in Table 1) are significant at a level better than 1%. This behavior may be adscribed to the decrease in the relative steric effects of methyl derivatives, with respect to allyl alcohol, on increasing surface area of supports. In agreement with this, Ni bulk would be expected to be the least selective catalyst because of the absence of whichever steric effect related to the support. However, the selectivity of unsupported nickel is higher than all nickel-supported catalysts, with the only exception of Ni/Al_2O_3. One consequence of this fact is that selectivity is not only governed by the textural properties of the supports.

On the other hand, changes in R with temperature are predicted by the classical theory of competitive hydrogenation (*29, 30*) and expected to follow an Arrhenius-type law. According to Tanaka and Chihara (*32*) this change may expressed by the relationship

$$R\,\frac{d(\ln R_{A,B})}{d(1/T)} = -(E_{a_A} - E_{a_B}) - (\omega_A - \omega_B), \qquad (3)$$

where ω and E_a are, respectively, the adsorption heat (negative values for exothermic) and apparent activation energies (energy required for bringing a substrate in the bulk solution up to the activated state on the catalyst surface). Thus, the temperature dependence of the relative reactivity, $R_{A,B}$, is given by the difference between the individual activation energies of the two reactions and the difference between the adsorption heats of both substrates A and B.

Considering the following formulation of the last expression:

$$R\,\frac{d(\ln R_{A,B})}{d(1/T)} = -(E_{a_A} + \omega_A) + (E_{a_B} + \omega_B) = -\Delta E_{\mathrm{true}_{A,B}}, \qquad (4)$$

where the quantity $(E_a + \omega)$ represents the energy required for bringing the adsorbed substrate to the activated state (true activation energy) we find that the dependence of R with temperature is determined by the difference between the true activation energies of both substrates. Thus, according to the results shown in Table 5 we have that the absence of change in R in the range of temperatures studied, may be adscribed to nearly identical values for ΔE_a and $\Delta\omega$. Thus, from (4) if $-\Delta E_a - \Delta\omega \simeq 0$ we have that

$$\Delta E_{a_{M,A}} \simeq -\Delta\omega_{M,A};$$

$$\Delta E_{a_{C,A}} \simeq -\Delta\omega_{C,A};$$

and

$$\Delta E_{a_{M,C}} \simeq \Delta\omega_{M,C}$$

for all studied catalysts.

On the other hand, the fact that in all cases $\Delta E_a \simeq -\Delta\omega$ ought to be interpreted as a Polanyi relationship (*33, 34*) which, applied to heterogeneous catalysts, states that the change in the Arrhenius activation energy in a series of simple related reactions from a first to a second reaction may be proportional to the change in the heat of adsorption; that is

$$\Delta E_a = -\alpha\Delta\omega, \qquad (5)$$

where α is a fraction between 0 and 1. In the present case we have obtained $\alpha \simeq 1$ as a consequence of the independence of R with temperature. However, the validity of the relationships (3) or (4) brings about the existence of a Polanyi relationship where the α value is related to the slope of ln R vs T^{-1}.

This pattern may be checked by the behavior of the relative adsorption constant, $K_{M,A}$, $K_{C,A}$, and $K_{M,C}$ with the temperature. In fact, we have that

$$K_{M,A} = \exp(\Delta S_{M,A}/R)\exp(-\Delta\omega_{M,A}/RT), \qquad (6)$$

where $\Delta S_{M,A}$ is the differential entropy of adsorption between allyl alcohol and its methyl derivative on the metal surface. Thus, we can obtain experimental values for $\Delta\omega_{M,A}$ and $\Delta S_{M,A}$ by plotting ln $K_{M,A}$ vs T^{-1} because

$$R\ln K_{M,A} = \Delta S_{M,A} - \Delta\omega_{M,A}T^{-1}. \qquad (7)$$

Table 6 collects values of $\Delta\omega_{M,A}$, $\Delta\omega_{C,A}$, and $\Delta\omega_{M,C}$ and their respective ΔS values. Also, the corresponding ΔE_a values are included. As may be seen, the values of ΔE_a and $\Delta\omega$ are practically coincidental. All values of $\Delta\omega$ for Ni/SiO_2 catalysts and those for $\Delta\omega_{M,C}$ with all catalysts, except Ni/Al_2O_3, are taken as zero due to the fact that there is no detectable change in K with the temperature. So in these cases, according to (7) the values of ΔS can be easily calcu-

TABLE 6

Experimental Values for $\Delta\omega$ and ΔE_a in kJ mol^{-1} and ΔS in kJ mol^{-1} K^{-1} in Different Pairs of Competing Reactants with Different Catalysts[a]

	Ni bulk	Ni/SiO_2	Ni/Al_2O_3	$Ni/AlPO_4$-F	$Ni/AlPO_4$-B	$Ni/AlPO_4$-P
$\Delta S_{M,A} \times 10^3$	62 ± 27	−24[b]	8 ± 3	−62 ± 3	24 ± 15	−84 ± 17
$\Delta\omega_{M,A}$	24.5 ± 8.3	0.0	−11.1 ± 0.9	−12.4 ± 0.8	14.8 ± 4.7	−19.0 ± 5.2
$\Delta E_{a_{M,A}}$	−23.1	−0.9	−11.2	11.6	−13.6	18.0
$\Delta S_{C,A} \times 10^3$	56 ± 3	−25[b]	24 ± 7	−54 ± 9	28 ± 14	−86 ± 12
$\Delta\omega_{C,A}$	24.7 ± 9.0	0.0	−15.9 ± 2.0	−9.8 ± 2.8	15.0 ± 4.4	−19.4 ± 3.6
$\Delta E_{a_{M,A}}$	−23.8	2.4	−15.5	11.7	−14.4	19.7
$\Delta S_{M,C} \times 10^3$	7[b]	1[b]	$-2.0 \pm 3 \times 10^{-3}$	-5×10^{-3}[b]	−0.4	0.2
$\Delta\omega_{M,C}$	0.0	0.0	−7.0 ± 0.9	0.0	0.0	0.0
$\Delta E_{a_{M,C}}$	0.7	−3.2	4.3	−0.1	0.8	−1.7

[a] Uncertainties are determined for a 95% confidence limit.

[b] These values of ΔS are determined from K values in Table 5.

lated from K values in Table 4 by

$$\Delta S = R \ln \bar{K}. \quad (8)$$

In these cases, the values of K are determined exclusively by the entropy factor ΔS, which may be adscribed to steric effects on the adsorption. Besides, the differential adsorption heats $\Delta\omega$ are closely related to the inductive effect of the substituent that changes the adsorption strength on the catalyst surface on changing the electronic density of the olefinic double bond.

Accordingly, from ΔS and $\Delta\omega$ values in Table 6 we can obtain every catalyst's relative contribution from both parameters (steric and inductive) in the relative adsorption constants $K_{M,A}$, $K_{C,A}$, and $K_{M,C}$, i.e., in the methyl substitution effects on adsorption. Previously, we have to consider that according to (7), the contribution of the entropy factor is given by $\Delta S/R$ while the influence of the differential adsorption heat is strongly determined by the temperature given by $-\Delta\omega/RT$. Therefore, the relative influence of steric and inductive effects is determined by the operating temperature. Since the reaction temperatures were in the range of 293–313 K, the value of $-\Delta\omega/RT$ have been obtained for $\bar{T} = 303$ K. The values thus obtained and those for $\Delta S/R$ are collected in Table 7.

These results may lead to the conclusion that the influence of the methyl group position is practically negligible; only with the catalyst Ni/Al_2O_3 was there a slight dependence of $K_{M,C}$ on temperature obtained. In order to evaluate the influence of methyl substitution on the different catalysts we have to take into account that as $K_{M,A}$ and $K_{C,A}$ values approach 1 the effects off the methyl substitution go down. Therefore, according to (7), as the positive value of $\Delta S/R$ and the negative value of $\Delta\omega/RT$ increase, the influence of the methyl effects decreases. Accordingly, under standard operating conditions the steric effect was decreased in the order $Ni/AlPO_4$-P > $Ni/AlPO_4$-F > Ni/SiO_2 > Ni/Al_2O_2 > Ni/Al_2O_3 > $Ni/AlPO_4$-B > Ni bulk, which is exactly the opposite of the inductive effect.

These results suggest that the steric ef-

TABLE 7

Contribution to the Relative Adsorption Constant K from the Relative Steric Hindrance ($\Delta S/R$) and from the Relative Adsorption Strengths ($\Delta\omega/RT$) in Every Studied Catalyst at 303 K

Catalyst	$\frac{\Delta S_{M,A}}{R}$	$\frac{\Delta\omega_{M,A}}{RT}$	$\frac{\Delta S_{C,A}}{R}$	$\frac{\Delta\omega_{C,A}}{RT}$	$\frac{\Delta S_{M,C}}{R}$	$\frac{\Delta\omega_{M,C}}{RT}$
Ni bulk	7.0	9.4	6.8	9.8	0.82	0.00
Ni/SiO_2	−2.4	−0.5	−3.0	0.0	0.95	0.84
Ni/Al_2O_3	1.0	4.4	2.9	6.3	−2.60	−2.81
$Ni/AlPO_4$-F	−7.5	−5.0	−6.5	−3.9	0.00	0.00
$Ni/AlPO_4$-B	2.9	5.9	3.4	5.9	0.05	0.00
$Ni/AlPO_4$-P	−10.3	−6.9	−10.4	−7.7	0.02	0.00

fects are increased and inductive effects diminished to a varied extent in the studied nickel catalysts due to the influence of the supports.

Compensation Effects

Furthermore, in all cases there is a compensation between the values of differential adsorption heat, $\Delta\omega_{M,A}$ and $\Delta\omega_{C,A}$, and entropy factors, $\Delta S_{M,A}$ and $\Delta S_{C,A}$, respectively, as shown in Fig. 3. In both cases linear regression coefficients above 0.99 with "*t*-tests" of significance in levels better than 1% are obtained.

According to Boudart (*33*) the general explanation of this fact and also of the obtained Polanyi relationship (5) is the existence of a linear free-energy relationship (LFER) which manifests itself in a linear relation between the enthalpy and entropy of adsorption for any set of reactions of the same type. A physical representation of the enthalpy–entropy relationship (*35*) is that the greater the binding energy of the molecule to the surface, then the more restricted the vibrational and rotational freedom.

From (7) we see that the slope of ΔS vs $\Delta\omega$ is $T^{-1} = \theta^{-1}$, a constant termed the "isokinetic temperature" or "θ temperature," which is the vibrational temperature of the reaction center (or core) of the active complex of adsorption (*36*). The values obtained from slopes in Fig. 3 are $\theta_{M,A} = 306 \pm 22$ K and $\theta_{C,A} = 312 \pm 9$ K.

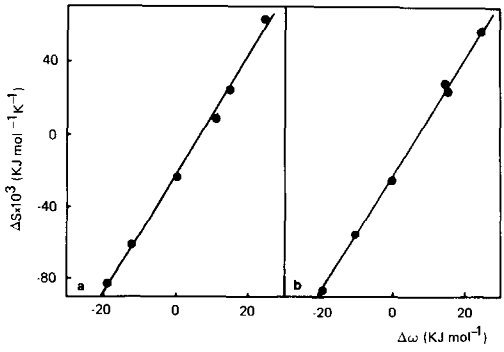

FIG. 3. Compensation effect between differential adsorption heats $\Delta\omega$ and entropy factors ΔS. (a) $\Delta S_{M,A}$ vs $\Delta\omega_{M,A}$ and (b) $\Delta S_{C,A}$ vs $\Delta\omega_{C,A}$.

TABLE 8

α and θ Values of Catalysts[a]

Catalyst	$\alpha_C \times 10^6$ (mol s^{-1} m$_{Ni}^{-2}$)	θ_C (K)
Ni bulk	0.3 ± 0.04	263 ± 27
Ni/SiO_2	13.2 ± 2.00	296 ± 34
Ni/Al_2O_3	4.1 ± 0.64	275 ± 46
$Ni/AlPO_4$-F	1242.0 ± 53.80	438 ± 12
$Ni/AlPO_4$-B	0.6 ± 0.07	260 ± 29
$Ni/AlPO_4$-P	134.2 ± 18.80	351 ± 34

[a] Uncertainties are determined for a 95% confidence limit.

However, the "compensation effect" is habitually obtained experimentally by a correlation between ln *A* and E_a from the Arrhenius expression (*37*) in the form

$$\ln A = \ln \alpha + E_a/\theta R, \qquad (9)$$

where θ is the isokinetic temperature at which identical values of areal rates $r_A = \alpha$ are obtained.

In fact, the plots of ln *A* vs E_a, in Table 3, for each catalyst, with the three substrates are linear with regression coefficients above 0.99. From the slopes and intercepts the α and θ parameters (α_C and θ_C) for all catalysts studied are obtained. They are shown in Table 8.

According to the Arrhenius expression, when *A* is expressed by Eq. (9) we have

$$r_A = \alpha \exp \frac{E_a}{R} (1/\theta - 1/T). \qquad (10)$$

Thus, below θ, the reactions with lower E_a exhibit higher reaction rates and, above θ, the inverse is true. According to this, we may justify the anomalous behavior previously indicated in the sequences for r_a with different catalysts in relation to their E_a values. Indeed, from results in Table 8 we find that in the experimental conditions of this study (293–313 K) with $Ni/AlPO_4$-P and -F, we operated below θ where low values of E_a enhance the catalytic activity. On the other hand, with unsupported Ni, Ni/Al_2O_3, and $Ni/AlPO_4$-B, we operated above θ and consequently high values of E_a enhance the catalytic activity. With Ni/SiO$_2$ we operated around θ. Furthermore, due to the support effects θ_C values are increased in the same order as $\Delta\omega_{M,A}$ and $\Delta\omega_{C,A}$ are diminished (Table 6). Since it was learned that the influence of inductive effects grows with increasing $\Delta\omega$ values, low values of θ_C ought to be associated with a high influence of inductive effects. This fact is in accord with what might be expected from Eq. (9) where the activity r_A is proportional to $\exp(\theta^{-1})$.

It should be noted that on plotting ln A vs E_a in all catalysts for every substrates (Fig. 4), we obtain straight lines with high correlation (0.99). From slopes and interceps we obtain the values of α_S and θ_S shown in Table 9 for allyl, methallyl, and crotyl alcohols. As may be seen, the θ_S values of M and C alcohols decrease from 354 to 274 and 279 K, respectively, due to the effects of methyl substitution. This fact may be clearly associated with the inductive effect of CH$_3$. It is interesting to note that the effects of the CH$_3$ substitution in α or β with respect to the functional group are very nearly coincidental.

Since α is catalytic activity at the temperature θ, it should be determined by E_a as well as by the production rate of transition surface intermediates which is closely related to the molecular geometry in α_S or to the number and characteristic of active sites in α_C. Thus, previous research found that on increasing the ring size from cyclopentane to cyclooctene, the α_S values decreased strongly and continuously, while, comparatively, the variation of θ_S was very small (*17*).

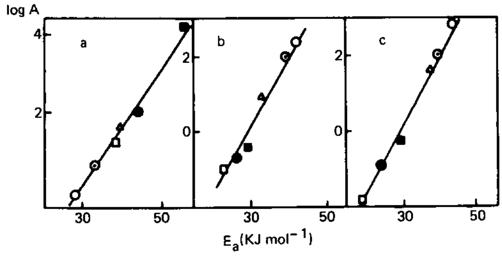

FIG. 4. Compensation effect between E_a and log A for (a) allyl alcohol, (b) methallyl alcohol, and (c) crotyl alcohol with all catalysts: (○) Ni/AlPO$_4$-P; (●) Ni/AlPO$_4$-B; (⊙) Ni/AlPO$_4$-F; (△) Ni/SiO$_2$; (□) Ni/Al$_2$O$_3$; and (■) Ni bulk.

TABLE 9

α and θ Values of Substrates[a]

Substrate	$\alpha_S \times 10^6$ (mol s^{-1} m$_{Ni}^{-2}$)	θ (K)
Allyl alcohol	153.8 ± 8.3	354 ± 13
Methallyl alcohol	1.6 ± 0.2	274 ± 27
Crotyl alcohol	2.4 ± 0.2	279 ± 19

[a] Uncertainties are determined for a 95% confidence limit.

Accordingly, we also have a compensation effect among the catalysts in the hydrogenation of the same substrates that likewise could be adscribed to an enthalpy–entropy relationship similar to that obtained by the effects of the methyl substitution in the competitive hydrogenation.

Finally, according to Boudart (*33*), the compensation effects obtained cannot be adscribed to a false correlation caused by scatter of data because θ_S and θ_C values are out of the range of temperatures covered by the experimental measurements. Besides, "*t*-tests" of significance, performed on the regression coefficients, show that these are significant at a level better than 1%. This is a measure of accuracy of fit of the data under the present experimental conditions.

CONCLUSIONS

On the basis of these results we may conclude that in the liquid-phase catalytic hydrogenation of the olefinic double bond with different substituents and on several supported nickel catalysts, we have a LFER due to the independence in true activation energy of these parameters (substituent and catalyst). As a consequence of this fact the enthalpy–entropy relationship obtained determines the relationship between ln A and E_a, termed compensation effect and the Polanyi relationship $\Delta E_a = -\Delta\omega$ shown in Fig. 5. Here we see that on going from A to B, where A and B are different catalysts or different substituents of the C=C bond, the true activation energy

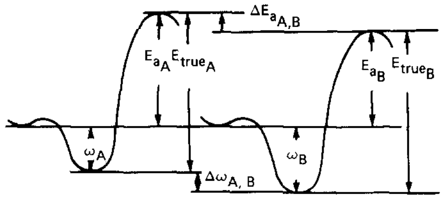

FIG. 5. Reaction coordinates in a Polanyi relationship where A and B are different catalysts or different substituents of the olefinic double bond and $\Delta E_a \simeq \Delta\omega$.

is unchanged and the differential $\Delta E_{a(A,B)} = E_{true(A)} - E_{true(B)}$ is identical to that of $-\Delta\omega_{A,B}$.

Furthermore, these conclusions may be supported by some already published results. Thus, on AlPO$_4$-supported rhodium catalysts we obtained the independence of the relative adsorption coefficients, R, from temperature (so that $\Delta E_{true} \simeq 0$) in the liquid-phase competitive hydrogenation of cyclohexene/cyclooctene (*17*) and styrene/α-methylstyrene (*16, 17*). In the competitive hydrogenation of styrene/α-methylstyrene on Ni/AlPO$_4$ (*10*) a slight change of $R_{MS,S}$ with the temperature was obtained although in all cases $\Delta E_{true} \leq 4$ kJ mol^{-1}, while ΔE_a was in the range 20–30 kJ mol^{-1}. Finally, $\Delta E_{true} < 1$ was obtained for Pt/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ and <3 for Ru/Al$_2$O$_3$ (*32*) in the liquid-phase competitive hydrogenation of cyclohexanone and its 2-alkyl derivatives (2-methyl, 2-ethyl, and 2-propyl cyclohexanone) on Ru/Al$_2$O$_3$, Rh/Al$_2$O$_3$, and Ru/Al$_2$O$_3$, using decalin as the solvent, in the temperature range of 268–341 K.

Accordingly, as far as the compensation effect is concerned, there seems to be a general pattern of behavior in the liquid-phase catalytic hydrogenation process, the parameters θ_C, α_C, θ_S, and α_S may provide a more general measurement of the reactivity characteristic of a series of related reactions and catalysts. Thus, only by taking into account the existence of a compensation effect in the studied reactions are we able to explain the sequences obtained in the catalytic activity of several studied catalysts; furthermore, we can make predictions on the relative influence of temperature conditions in every catalyst and substrate studied.

Finally, we may conclude that the method of preparation of AlPO$_4$ strongly influences not only the metal–support interaction but also the metallic dispersion. Thus, while the dispersion decreases in the sequence Ni/AlPO$_4$-B > Ni/AlPO$_4$-F > Ni/AlPO$_4$-P, by contrast, the areal rate increases in the opposite order. As a consequence of both influences, the catalytic activity per gram of supported metal nickel (obtained in Table 1 as the product of S by r_A) decreases in the order F > P > B. So we find that ammonia is the best precipitation agent in the synthesis of AlPO$_4$ by the Kearby method. Likewise, we see that the activity per unit weight of nickel metal deposited in the reduction of allyl alcohol follows the sequence Ni/AlPO$_4$-F > Ni/AlPO$_4$-P > Ni/SiO$_2$ > Ni/AlPO$_4$-B $\gg$ Ni/Al$_2$O$_3$ $\gg$ Ni; while in the methyl derivatives it is Ni/SiO$_2$ > Ni/AlPO$_4$-F > Ni/AlPO$_4$-P > Ni/AlPO$_4$-B $\gg$ Ni/Al$_2$O$_3$ $\gg$ Ni.

So the present results show not only the importance of the role of the support in determining the adsorption and catalytic behavior of supported nickel systems but also the excellent behavior of several aluminum phosphates as nickel supports.

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