Gas-phase oxydehydrogenation of ethylbenzene with nitrobenzene by hydrogen transfer catalyzed reaction to produce styrene and aniline

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Gas-phase catalytic hydrogen transfer reaction between ethylbenzene and nitrobenzene, to produce styrene and aniline, has been carried out at 360–460 °C on amorphous $AlPO_4$, SiO_2, Al_2O_3, and on a natural sepiolite, as well as on the corresponding 20 wt% supported nickel catalysts. The influence of Cu as a second metal was also studied. Reactions were also carried out without nitrobenzene, under nonoxidative conditions. Catalytic activity under oxidative conditions was always comparatively higher than in nonoxidative conditions. In both cases, styrene yield and selectivity values obtained with support materials directly used as catalysts were better than those obtained with the corresponding Ni or Ni–Cu supported metal catalysts, with the only exception of SiO_2. The best results were obtained when amorphous $AlPO_4$ was used as the catalyst. The catalytic activity obtained in both oxidative and nonoxidative conditions, was closely associated to acid–base properties of the catalysts studied. Furthermore, a very similar linear correlation between $\ln A$ and E_a known as "compensation effect" was obtained and a common dehydrogenation mechanism was considered for oxidative and nonoxidative conditions. However, without considering the catalyst, nitrobenzene plays an important role as hydrogen acceptor, not only shifting the ethylbenzene dehydrogenation equilibrium but also avoiding secondary reactions by lowering the level of available hydrogen, especially when supported metals are being used as catalysts.

Keywords: ethylbenzene oxydehydrogenation, nitrobenzene as oxidant, hydrogen transfer reaction, amorphous $AlPO_4$, supported nickel catalysts, acid–base properties, compensation effect

1. Introduction

Styrene is industrially produced by dehydrogenation of ethylbenzene in vapor phase on several iron oxide catalysts at 600–700 °C, just below where thermal cracking becomes significant. Due to its high endothermic character, superheated steam is used to provide the thermodynamic driving force of the reaction as well as to reduce the partial pressure of substrates and to reduce coking to keep the catalyst clean and active [1]. The provision of the necessary process heat can be carried out better by the concurrent use of an exothermic reaction to drive the ethylbenzene dehydrogenation. Thus, oxidative dehydrogenation of paraffins and alkylbenzenes through an exothermic process at lower reaction temperatures has attracted considerable attention and the use of oxygen as the hydrogen acceptor yielding water as a by-product has been the subject of much research [2,3]. Besides, other oxidative systems such as iodine, sulphur dioxide or sulphur, generated by the reaction between hydrogen sulfide and oxygen, have also been studied [4,5]. Despite the good results obtained, commercial development of a process to manufacture styrene by SO_2 dehydrogenation of ethylbenzene has not been realized due to problems in catalyst deactivation [6]. More recently, nitrobenzene has also been studied in the catalytic oxidative dehydrogenation of ethylbenzene to form styrene and aniline [7–9]:

$$3C_6H_5\text{–}CH_2\text{–}CH_3 + C_6H_5\text{–}NO_2 \rightarrow 3C_6H_5\text{–}CH{=}CH_2 + C_6H_5\text{–}NH_2 + 2H_2O \quad (1)$$

Taking into account that styrene and aniline are commercially interesting products, the selection of suitable catalysts is required for improving the yield and selectivity of both reaction products. With respect to this, supported metal catalysts are not only able to carry out nitrobenzene hydrogenation but also to produce ethylbenzene dehydrogenation through the reversal of the steps of a classical Horiuti–Polanyi type mechanism describing the hydrogenation of an olefinic double bond. Thus, we have previously studied the nonoxidative [10,11] and oxidative [12,13] dehydrogenation of alkylbenzenes on both $Ni/AlPO_4$ and $Rh/AlPO_4$ supported catalysts as well as on $AlPO_4$ and some oxides such as SiO_2 and Al_2O_3 [14]. In this regard, due to its high surface area, thermal stability and surface acid–base properties, we have previously reported the use of amorphous $AlPO_4$ not only as a metal support [15–19], but also as a heterogeneous catalyst in the field of selective organic chemistry in fine chemistry [20–28].

The present study reports the results obtained when several supported nickel catalysts, previously studied in the liquid-phase hydrogenation of alkynes [18,19], are used in

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the gas-phase catalytic hydrogen transfer reaction between ethylbenzene and nitrobenzene, to produce styrene and aniline. Support effects and the influence of Cu as a second metal are also studied.

2. Experimental

2.1. Catalysts

Some catalysts used were previously described in the liquid-phase hydrogenation of 1,4-butynediol [18] and phenylacetylene [19]. These catalysts, containing 20 wt% nickel, were prepared by impregnation of the supports to incipient wetness with 10 M aqueous nickel nitrate, following the procedure previously described [10–19]. They were dried, crushed and screened to particle size <0.149 mm (10 mesh size), reduced in an ultrapure hydrogen stream (1.7 $cm^3\,s^{-1}$) at 400 °C for 4 h, and then cooled to room temperature in the same hydrogen stream.

Amorphous $AlPO_4$ was obtained according to the sol–gel method previously described [10–28]. This support was prepared by precipitation from aqueous solutions of $AlCl_3{\cdot}6H_2O$ and H_3PO_4 (85 wt%) at pH = 6.1 at the "precipitation end point", with ammonium hydroxide solution. The solid obtained was then washed with isopropyl alcohol and dried at 120 °C for 24 h. The resulting powder screened at 0.120–0.149 mm was calcined for 3 h in an electric muffle furnace at 650 °C. Furthermore, some habitual commercial materials such as a silica from Merck (Kieselgel 60, 70–230 mesh), SiO_2, an alumina (aluminum oxide active acidic for chromatography) from Merck, Al_2O_3, as well as natural sepiolite from Vallecas (Madrid), supplied by Tolsa S.A., Sep, were also used as supports, after undergoing the same calcination treatment. In addition, in order to evaluate the role of Cu in Ni–Cu alloying, two Ni–Cu bimetallic systems, containing Ni 20 wt% and Cu 0.3 wt%, were prepared using $AlPO_4$ and Sep as supports. In these bimetallic catalysts copper nitrate was also used in the impregnation step. Besides, four commercial nickel catalysts from Harshaw-Chemie B.V. were used as references: Ni-5333 T (20 wt% Ni), Ni-5132 P (64 wt% Ni), Ni-3210 T (35 wt% Ni) and Ni-6458 T (60 wt% Ni).

The metal surface area, S_{Ni}, of the supported nickel catalysts was obtained from the average crystallite size diameter, D, determined by X-ray diffraction according to the method of Moss [29] by using the classical Scherrer equation [30], as has been described elsewhere [10–19]. X-ray powder diffraction patterns were recorded with a Siemens D500 diffractometer working with Cu K_α radiation monochromated by a graphite crystal. The data collection was performed with a DACO-MP system. The profiles were recorded by the "step scan" technique with a step width of 0.02° 2θ. Background was automatically corrected by the DACO-MP system and α_2-elimination was carried out by the Rachinger method [31]. Metal surface area, S_{Ni}, and average crystallite diameters, D, of supported nickel catalysts are shown in table 1. Surface area of supports and supported nickel catalysts, S_{BET}, determined by nitrogen adsorption [10,12,14,18–20] are also summarized in table 1, where the surface basicity and acidity are also collected. These values were determined by a spectrophotometric method described elsewhere [21], that allows titration of the amount of irreversibly adsorbed benzoic acid (BA, $pK_a = 4.19$) or pyridine (PY, $pK_a = 5.25$) employed as titrant agents of basic and acid sites, respectively. The monolayer coverage at equilibrium at 25 °C, X_m (μmol g^{-1}), is accomplished by applying the Langmuir adsorption isotherm, and is assumed as a measure of the acid or basic sites corresponding to the specific pK_a of the base or acid used as the titrant. In fact, the spectrophotometric method employed lets us determine not only the surface acidity and basicity of white solids such as the supports, but also the black ones such as the nickel supported catalysts.

Table 1
Surface area, S_{BET}, and acid–base properties of different catalysts as well as crystallite diameter, D, and metal surface area, S_{Ni}, of supported metal catalysts.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	Acidity vs. PY (μmol g^{-1})	Basicity vs. BA (μmol g^{-1})	D (nm)	S_{Ni} ($m^2\,g^{-1}$)
$AlPO_4$	156	190	200	–	–
Al_2O_3	72	23	191	–	–
SiO_2	366	206	164	–	–
Sep	203	31	174	–	–
$Ni/AlPO_4$	78	40	159	15.0	45
Ni/Al_2O_3	60	15	178	10.7	63
Ni/SiO_2	264	106	82	11.4	59
Ni/Sep	102	32	124	9.2	73
$Ni–Cu/AlPO_4$	65	42	142	10.4	65
Ni–Cu/Sep	103	31	132	8.8	77

2.2. Catalytic measurements

Oxidative dehydrogenation reactions were carried out in a conventional fixed-bed type reactor, previously described [10–14], made of quartz with a continuous flow system, at atmospheric pressure and in the temperature range 360–460 °C. By means of a microfeeder, a mixed stream of ethylbenzene (EB) and nitrobenzene (NB), EB/NB = 3, with a feed rate $F = 6$ ml/h was administered after dilution with dried nitrogen at a flow rate of 30 ml/min in 0.3 g of catalyst weight. The chromatographically pure ethylbenzene and nitrobenzene were used as supplied by Merck, p.a. after distillation under reduced pressure and low temperature. Besides, the screening of the catalysts was also carried out under nonoxidative conditions, where the same standard reaction conditions were fixed but without NB in the feed stream. Different catalyst weights to obtain different residence time values, W/F, as well as different EB/NB molar ratios (figure 1) were also studied. Times on stream of 90 min (figure 1) were developed with all catalysts stud-

ied. The reaction liquid products collected by traps cooled with dry ice were analyzed by GC with FID by using a column (2 m × 0.3 mm) packed with 5% polyphenylether on Chromosorb G AW-DMCS 80/100 at 130 °C. In addition to styrene (ST) and aniline (AN), always obtained with high selectivity, reaction by-products (Byprod) on the different catalysts were found to be benzene (B), nitrosobenzene (NSB) and in minor amounts, toluene (T). A sum of all these was used because the amounts of these by-products were quite small in most cases. Furthermore, thermal reaction was negligible.

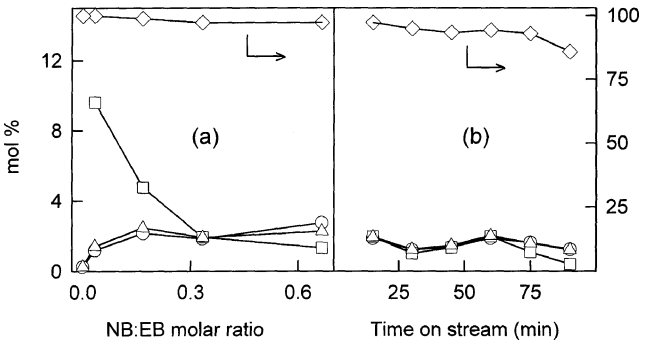

Figure 1. Influence of the NB : EB ratio (a) and time on stream (b), on the conversion (○), styrene yield (△), aniline yield (□) and selectivity (◇), on $AlPO_4$ catalyst at standard reaction conditions and $T = 420\,°C$.

3. Results and discussion

Experiments carried out with some selected catalysts indicated, according to the results previously obtained [10–14], that the absence of external diffusion effects is obtained for residence time values, W/F, down to 0.077 h. In this interval, a first-order rate equation is found to fit the data, so that we can apply the "differential reactor" conditions for the treatment of the rate data. The average particle size of catalysts studied (<0.149 mm) also determines that reactions were not influenced by internal diffusional limitations. Thus, under oxidative conditions with EB/NB = 3, the standard working conditions to carry out the reaction test for each catalyst studied were $W/F = 0.062$ h, with $W = 0.3$ g, at three different temperatures: 360, 420 and 460 °C. Under nonoxidative conditions, without NB in the feed stream, the same standard reaction conditions and temperatures were used with a very closely similar $W/F = 0.058$ h. From the reaction products obtained at 1 h of time on stream, several kinetic parameters are defined and their corresponding values for different catalysts and temperatures are compiled in tables 2 and 3.

Table 2
Catalytic performance of different systems under standard reaction conditions at different temperatures and under oxidative and nonoxidative conditions.

Catalyst	T	Without nitrobenzene			With nitrobenzene			
	(°C)	Y_S	C	S	Y_S	Y_A	C	S
$AlPO_4$	360	0.26	0.26	100.0	1.85	1.94	1.92	97.3
	420	0.51	0.53	96.0	5.83	10.79	7.36	90.7
	460	0.63	0.72	88.2	8.56	17.17	12.62	76.4
Al_2O_3	360	0.08	0.08	100.0	0.59	1.87	1.04	85.1
	420	0.46	0.47	97.7	1.60	2.94	3.24	58.2
	460	0.79	0.83	96.2	2.45	3.84	7.14	36.7
SiO_2	360	0.02	0.02	100.0	0.07	0.00	0.21	24.4
	420	0.12	0.15	79.3	0.71	0.53	1.95	34.0
	460	0.36	0.39	91.8	2.86	4.42	7.94	38.1
Sep	360	0.92	0.93	98.9	1.42	0.97	1.41	94.4
	420	1.32	1.35	98.4	3.11	4.50	4.17	80.4
	460	1.51	1.58	95.6	4.64	3.84	6.67	66.1
$Ni/AlPO_4$	360	0.12	0.35	34.8	1.06	12.58	3.55	85.9
	420	0.35	3.54	9.8	2.73	29.10	10.63	59.6
	460	0.92	6.64	13.9	6.29	62.34	28.12	35.3
Ni/Al_2O_3	360	0.12	0.44	27.8	0.26	7.53	2.52	74.8
	420	0.49	5.42	9.0	0.71	10.30	4.42	69.0
	460	0.95	5.13	18.4	1.65	12.32	9.19	37.7
Ni/SiO_2	360	0.37	0.80	46.3	0.73	13.05	3.82	89.7
	420	0.88	1.47	59.6	1.68	23.47	8.30	69.0
	460	1.32	1.75	75.4	2.62	16.07	9.10	53.8
Ni/Sep	360	0.05	0.56	9.1	0.52	5.82	1.74	95.5
	420	0.36	2.07	17.2	0.97	16.81	5.13	82.1
	460	1.34	2.17	62.0	2.02	28.86	9.98	67.6
$Ni–Cu/AlPO_4$	360	0.22	0.36	61.1	1.00	11.80	3.73	90.5
	420	0.37	0.64	57.1	2.48	23.13	7.97	82.2
	460	0.63	1.60	39.5	4.33	25.01	10.94	70.0
Ni–Cu/Sep	360	0.10	0.40	25.0	0.89	4.89	2.06	83.0
	420	0.22	1.06	21.1	1.94	27.06	9.09	74.1
	460	0.43	2.03	21.2	3.91	26.65	13.03	51.2

Table 3
Catalytic performance of Harshaw commercial catalysts under standard reaction conditions at different temperatures and under oxidative and nonoxidative conditions.

Catalyst	T	Without nitrobenzene			With nitrobenzene			
	(°C)	Y_S	C	S	Y_S	Y_A	C	S
Cu-3820-P	360	0.79	0.86	92.8	0.17	7.04	2.09	93.8
	420	1.11	1.15	96.9	0.45	3.91	2.13	58.4
	460	1.60	1.62	98.6	1.02	1.94	4.86	24.1
Ni-5333-T	360	0.15	1.83	8.4	0.44	0.37	0.73	78.4
	420	0.39	2.14	18.1	0.73	27.46	8.56	67.1
	460	0.62	2.51	24.7	1.37	25.36	8.91	61.9
Ni-3210-T	360	0.13	3.29	4.1	0.56	11.14	3.31	85.9
	420	0.25	1.48	17.2	0.93	36.17	9.50	87.1
	460	0.56	2.22	25.3	1.37	25.36	8.91	61.9
Ni-5132-P	360	0.05	3.86	1.3	0.95	36.77	14.09	57.5
	420	0.14	9.20	1.5	1.83	77.70	19.60	79.5
	460	0.19	11.41	1.7	2.55	76.61	18.69	81.7
Ni-6458-T	360	0.04	4.02	1.0	0.69	57.74	14.78	72.0
	420	0.15	10.42	1.5	1.62	50.06	14.92	64.1
	460	0.23	12.61	1.8	3.33	29.57	13.34	55.7

In this connection, styrene and aniline yields, Y_S and Y_A, conversion, C, and selectivity, S, are calculated from the following expressions:

$$Y_S = \frac{\text{ST}}{\text{EB} + \text{ST}} \times 100 \quad \text{and} \quad Y_A = \frac{\text{AN}}{\text{NB} + \text{AN}} \times 100, \tag{2}$$

$$C = \frac{\text{ST} + \text{AN} + \text{Byprod}}{\text{EB} + \text{NB} + \text{ST} + \text{AN} + \text{Byprod}} \times 100, \tag{3}$$

$$S = \frac{\text{ST} + \text{AN}}{\text{ST} + \text{AN} + \text{Byprod}} \times 100. \tag{4}$$

Results in figure 1 showing the influence of EB/NB ratio and time on stream on these kinetic parameters are similar to those obtained with all catalysts studied. Thus, it can be seen in figure 1(a) that C and Y_S increase and Y_A decreases on increasing the amount of NB in stream to NB/EB = 0.167, where the values of C, Y_S and Y_A are closely similar, which is when the molar ratio EB/NB = 3 is obtained, such as corresponds in equation (1). The very high selectivity obtained is practically unchanged using different amounts of NB in stream. Consequently, the presence of NB mixed with EB in the feed stream clearly increases C and Y_S values, according to results collected in tables 2 and 3, where, depending on the catalyst, these parameters can be increased by a factor higher than ten, as can be seen in figure 2. This is especially true with $AlPO_4$, the best catalyst. However, contrary to what was obtained when oxygen was used as the hydrogen acceptor [12], in the present case using NB as the oxidant, the Y_S and S values obtained with $AlPO_4$ directly used as the catalyst are better than those obtained with the corresponding $Ni/AlPO_4$ and $Ni–Cu/AlPO_4$ supported metal catalysts. This also happens with sepiolite and Al_2O_3 (figure 2). Only Ni/SiO_2 was better than the SiO_2 support alone, under oxidative conditions. Under nonoxidative conditions, only sepiolite exhibited this behavior and was better than Ni/Sep and Ni–Cu/Sep catalysts. The presence of supported nickel metal also promotes an important decrease in S with respect to the corresponding support alone, with the sole exception of Ni/SiO_2 under oxidative conditions.

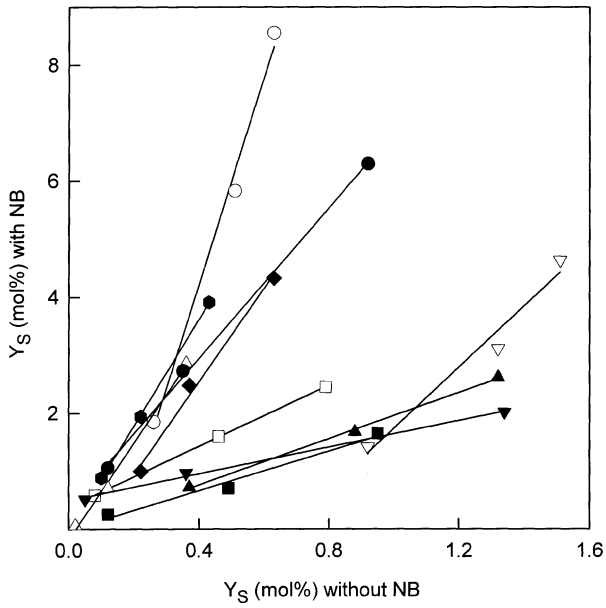

Figure 2. Influence of nitrobenzene (NB) in the the styrene yield, Y_S, obtained under standard reaction conditions at different temperatures and on different catalysts: (○) $AlPO_4$; (□) Al_2O_3; (△) SiO_2; (▽) Sep; (●) $Ni/AlPO_4$; (■) Ni/Al_2O_3; (▲) Ni/SiO_2; (▼) Sep; (◆) Ni–Cu/$AlPO_4$; and (⬢) Ni–Cu/Sep.

According to results obtained from table 2, in nickel supported catalysts when NB is used as the oxidant, Y_A values experience an important enhancement and also the S values increase. The incorporation of Cu as a second metal enhances S for moderate values of C, Y_S and Y_A. These results are consistent with those obtained with commercial metal supported catalysts (table 3). Here we have to point out the catalyst Ni-5132-P, which is able to obtain 20% in C, with 80% in S and Y_A as well as with only 2% in Y_S. Thus, by opposite to the irreversible character of the hydrogenation reaction of NB to AN, the re-

versible character of the ST/EB conversion, through hydrogenation/dehydrogenation, may clearly determine the low proportion ST/NB always obtained. In fact, the differences shown in figure 3, on plotting Y_A in respect to Y_S values, between Ni supported catalysts and the corresponding supports used as catalysts, can be explained from the more easy hydrogenation reaction of ST and NB on Ni catalysts than on support surfaces. Consequently, a bifunctional mechanism in which ST is formed on the support surface as well as on the Ni surface and subsequently hydrogenated on the Ni supported surface could explain the lower proportion ST/AN obtained in metal supported catalysts in respect to the supports.

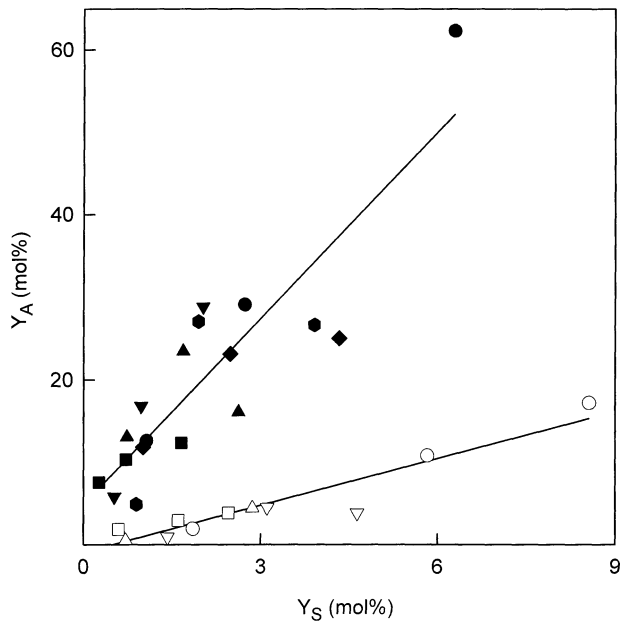

Figure 3. Differences obtained between supports and Ni supported catalysts in the aniline and styrene yields (Y_A and Y_S) under oxidative standard reaction conditions at different temperatures: (○) $AlPO_4$; (□) Al_2O_3; (△) SiO_2; (▽) Sep; (●) $Ni/AlPO_4$; (■) Ni/Al_2O_3; (▲) Ni/SiO_2; (▼) Sep; (⧫) Ni–Cu/$AlPO_4$; and (⬢) Ni–Cu/Sep.

Nickel seems to promote secondary reactions in the dehydrogenation of ethylbenzene but, at the same time, by acting as a hydrogenation catalyst, is able to increase the transformation of NB to valuable AN. Independently of the catalyst, NB plays an important role as a hydrogen acceptor, not only shifting the ethylbenzene dehydrogenation equilibrium but also due to the fact that a lower level of hydrogen avoids secondary reactions, especially when supported metals are used as catalysts.

From the results obtained in the temperature range studied (tables 2 and 3) the apparent activation energies, E_a, and Arhenius constants, $\ln A$, were obtained from the slope and intercepts of $\ln k$ vs. $1/T$, according to the Arrhenius equation. The specific reaction rate constant values, k_S ($\mathrm{mol\,s^{-1}\,g^{-1}}$), were obtained from the product $(Y_S \times F)/100$, where F is the ethylbenzene feed rate ($\mathrm{mol\,s^{-1}\,g^{-1}}$). Results are shown in table 4. Like that obtained when oxygen was used as the oxidant [12,13], a "compensation effect" or "isokinetic relationship" [32–37] exists (figure 2), according to the most habitual representation:

$$\ln A = \ln \alpha + E_a/\Theta, \tag{5}$$

where R is the gas constant, Θ the isokinetic temperature at which identical values of the reaction rate constant α are obtained. Thus, the values of both isokinetic parameters (Θ and $\ln \alpha$) were obtained, for oxidative and nonoxidative conditions, from slopes and intercepts in figure 4. It is interesting to note that on plotting the corresponding E_a and $\ln A$ values with all catalysts studied in table 4, not only very good regression coefficients were obtained, 0.993 and 0.996, respectively, for both kinds of reactions studied, but also the corresponding values of isokinetic parameters were closely similar. Thus, under oxida-

Table 4
Apparent activation energies, E_a ($\mathrm{kJ\,mol^{-1}}$), and Arrhenius constant, $\ln A$ ($\mathrm{mol\,s^{-1}\,g^{-1}}$), as well as correlation coefficient, r, for different catalysts. Uncertainties are also determined by standard deviations.

Catalyst	Without nitrobenzene			With nitrobenzene		
	E_a	$\ln A$	r	E_a	$\ln A$	r
$AlPO_4$	35.1 ± 4.9	-9.5 ± 1.3	0.99	60.3 ± 7.6	-2.7 ± 1.4	0.99
Al_2O_3	90.4 ± 12.9	-0.1 ± 2.3	0.99	55.6 ± 4.1	-4.8 ± 0.7	1.00
SiO_2	111.8 ± 1.9	2.4 ± 0.1	1.00	142.9 ± 1.6	9.6 ± 0.3	1.00
Sep	19.5 ± 2.0	-11.2 ± 1.1	0.99	45.9 ± 1.4	-5.8 ± 0.3	1.00
$Ni/AlPO_4$	77.1 ± 9.7	-2.4 ± 1.7	0.99	67.5 ± 8.0	-2.0 ± 1.4	0.99
Ni/Al_2O_3	80.5 ± 4.1	-1.7 ± 0.7	1.00	70.2 ± 7.3	-2.9 ± 1.3	0.99
Ni/SiO_2	49.7 ± 2.6	-6.4 ± 0.3	1.00	49.5 ± 1.0	-5.8 ± 0.2	1.00
Ni/Sep	126.2 ± 4.9	6.1 ± 0.9	1.00	50.8 ± 10.3	-5.9 ± 1.8	0.98
Ni–Cu/$AlPO_4$	39.8 ± 6.5	-8.9 ± 1.4	0.99	56.4 ± 1.0	-4.1 ± 0.2	1.00
Ni–Cu/Sep	55.7 ± 6.0	-6.7 ± 0.7	0.99	56.0 ± 7.0	-4.4 ± 1.2	0.99
Cu-3820-P	26.5 ± 4.7	-10.1 ± 0.8	0.98	68.4 ± 7.2	-3.7 ± 0.4	0.99
Ni-5333-T	55.4 ± 2.4	-6.3 ± 0.3	1.00	42.6 ± 9.4	-7.7 ± 1.7	0.98
Ni-3210-T	54.5 ± 11.9	-6.6 ± 2.1	0.98	34.1 ± 2.6	-9.0 ± 0.5	1.00
Ni-5132-P	53.0 ± 8.0	-7.8 ± 1.2	0.99	38.5 ± 1.3	-7.6 ± 0.3	1.00
Ni-6458-T	69.3 ± 9.3	-4.9 ± 0.7	0.99	59.8 ± 6.3	-3.9 ± 1.1	0.99

Table 5
Results for the single regression models ($y = ax + b$) between some surface properties of catalysts, in table 1, and their kinetic parameters obtained under oxidative and nonoxidative conditions, in table 2, as well as the corresponding significance levels and uncertainties determined by standard deviations.

Conditions	y	x	a	b	Significance (%)
Nonoxidative	Y_S	S_{BET}/PY	0.15 ± 0.06	0.09 ± 0.03	96.5
Nonoxidative	$\ln S$	$1/S_{BET}$	-104 ± 58	4.7 ± 2.6	90.0
Oxidative	Y_S	PY/S_{BET}	3.7 ± 1.2	0.5 ± 0.1	98.4
Oxidative	Y_A	BA	-0.18 ± 0.08	43 ± 19	94.3
Oxidative	$\ln S$	S_{BET}	$-1.6 \times 10^{-3} \pm 0.8 \times 10^{-3}$	4.5 ± 2.3	91.3

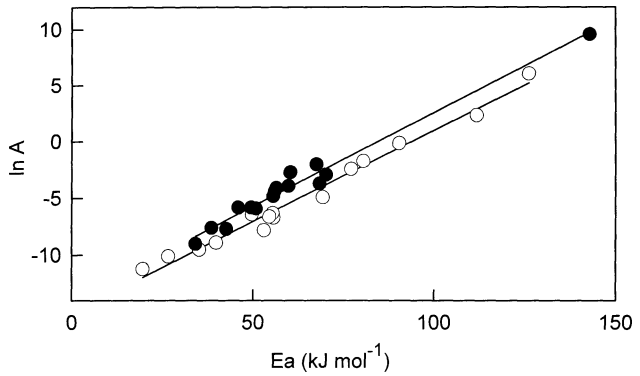

Figure 4. Compensation effect between E_a and $\ln A$ for dehydrogenation of ethylbenzene under nonoxidative conditions (○) and under oxidative conditions by using nitrobenzene as the oxidizing agent (●).

tive conditions $\Theta = 477 \pm 31\,^{\circ}C$, and $\ln \alpha = -13.5 \pm 0.6$, while under nonoxidative conditions, without NB in the feed stream, they take the values $\Theta = 475 \pm 25\,^{\circ}C$ and $\ln \alpha = -15.0 \pm 0.5$.

Furthermore, if a compensation effect holds for a reaction series, exhibiting similar isokinetic parameters, a single common interaction mechanism can be expected [32–37]. In this respect, the results shown in figure 2 manifest the existence of an identical mechanism in the dehydrogenation reaction of ethylbenzene to styrene, under nonoxidative conditions and in the presence of NB as the oxidant. Unlike that obtained here, using oxygen as the oxidant [12,13] different isokinetic parameters were obtained which imply the existence of important differences in the EB dehydrogenation reaction that were ascribed to the direct participation of an activated triplet oxygen molecule in the activated complex. In the present case, when NB is present we have two parallel reactions, where the same catalyst is able to promote the alkane dehydrogenation process as well as the hydrogenation of NB by using the hydrogen obtained in the parallel dehydrogenation reaction.

However, in order to determine the potential influence of textural acid–base properties of catalysts on the catalytic properties, we developed a correlation matrix by using all the data in table 1 and those corresponding to 420 °C in table 2. The values of the slopes and intercepts obtained in the regression analysis of those well-correlated parameter pairs are collected in table 5, where the corresponding significance levels are also indicated. According to the results previously obtained when oxygen was used as the oxidant [14], the results collected in table 5 showed a very good correlation between ST production and the specific acidity values, obtained through the quotients PY/S_{BET}, which represent the surface density of acid sites of catalysts. The number of surface basic sites on catalysts, BA, promote a negative influence on AN yield. In contrast, under nonoxidative conditions, ST yield was related to the inverse of the surface density of acid sites, S_{BET}/PY. Similarly, the more complex relationship obtained between the selectivity, $\ln S$ and S_{BET} of the catalyst, was also the inverse, depending on oxidative or nonoxidative operating conditions.

The role of acid sites in favoring the production of olefins through the oxydehydrogenation process has been emphasized [38]. In these reactions, product formation occurs via the homolytic abstraction of hydrogen atoms from the adsorbed reactant intermediates which takes place on Lewis acid sites [39]. In EB oxydehydrogenation, the role of acid sites can also be associated to the formation of catalytically active coke [40–43]. However, we have also considered the existence of another concerted mechanism carried out directly on the Lewis acid sites of the catalyst [12]. Thus, instead of dehydrogenation mechanisms of EB seeming to be different with NB or O_2, the same textural and acid–base properties of solid surfaces are adequate to obtain the best catalysts in the hydrogenation transfer reaction. Another important difference is the role of supported nickel, which enhanced the catalytic behavior of supports when oxygen was used as a hydrogen acceptor [12], but in the present case, when NB was used as the oxidant, the Y_S and S values obtained with supports directly used as catalysts are better than those obtained with the corresponding Ni or Ni–Cu supported metal catalysts. Only Ni/SiO_2 was better than the SiO_2 support alone, with NB used as the oxidant.

4. Conclusions

According to the results, we may conclude that, similar to the oxidative dehydrogenation of ethylbenzene with oxygen [14], the density of surface acid sites of catalysts also plays an important role when nitrobenzene was used as the oxidant. However, in the present case, the existence of a common isokinetic relationship with the nonoxidative process prompts us to consider a single common mechanism, contrary to what was obtained when oxygen was

used as the oxidant [12]. Thus, here we have NB working, in fact, like a hydrogen "cleaner" in a parallel hydrogenation reaction where AN was obtained with a yield higher than styrene. In this reaction, $AlPO_4$ alone, without any supported metal, was the best catalyst in obtaining ST with a high selectivity. $Ni/AlPO_4$ catalysts also promoted the highest conversion values, but as in all nickel-supported catalysts, selectivity was lowered by cracking secondary reactions developed on metal Ni surface.

Consequently, the results here obtained indicate the possibility of using $AlPO_4$ as a catalyst, or as a component of a catalyst, to obtain dehydrogenation of ethylbenzene with the aid of nitrobenzene as an "additive", to increase selectivity to styrene and operating at lower reaction temperatures than actually used in the nonoxidative process. Besides, the results obtained also indicate the possibility of obtaining the gas-phase hydrogenation of nitrobenzene with some cheap hydrocarbon, instead of using hydrogen in liquid phase. A tailored $Ni–Cu/AlPO_4$ supported metal catalyst could be a good candidate. Besides, in this sense results obtained with the Harshaw commercial catalyst Ni-5132-P were already very interesting, taking into account that 78% AN yield was obtained with 80% selectivity.

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