Gas-Phase Dehydrogenation of Alkylbenzenes on Rh/AlPO$_4$ Catalysts

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(Received March 1, 1989)

The nonoxidative dehydrogenation of alkylbenzenes (ethylbenzene, propylbenzene, and isopropylbenzene) has been carried out at 693—853 K on rhodium catalysts at 1 wt% supported on two different types of AlPO$_4$. In similar experimental conditions, the specific catalytic activity of the Rh/AlPO$_4$ catalysts is higher than that obtained previously for Ni/AlPO$_4$ (20 wt%) catalysts. Besides, a linear free energy relationship (LFER) was also obtained, manifesting itself through a "compensation effect" between the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ activation parameters obtained from the Eyring equation (and between $\ln A$ and E_a, from the Arrhenius equation). Furthermore, no extensive metal-support interaction effect was obtained as in the case of Ni/AlPO$_4$ catalysts in spite of exhibiting the same concerted mechanism previously described for the nonoxidative dehydrogenation of alkylbenzenes on supported nickel catalysts.

The dehydrogenation of ethylbenzene to styrene is a very important industrial reaction actually carried out in the vapor phase on iron oxide stabilized with several promotors in the presence of water vapor.[1] However, considerable work has been done in recent years to produce other catalysts such as metallic oxides,[2–4] several oxide salts[5–7] or supported metal catalysts.[8–10] With respect to the latter we studied[11] the nonoxidative dehydrogenation of several alkylbenzenes at 673—823 K on nickel catalysts at 20 wt% supported on Al_2O_3, SiO_2, and two different types of AlPO$_4$ synthesized according to Kearby.[12] Acid and basic sites did not exhibit catalytic activity. However, the acid-basic nature of the supports, through the effects of a strong metal-support interaction were found to play an important part in determining the catalytic activity of the supported nickel catalysts. These metal-support interaction effects were evaluated through several isokinetic parameters obtained from the existence of a linear correlation between the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ activation parameters obtained from the Eyring equation (and between $\ln A$ and E_a, from the Arrhenius equation) known as the compensation effect.

These metal-support interaction effects were previously obtained in the liquid-phase hydrogenation of the olefinic double bond on AlPO$_4$-supported nickel[13–15] and rhodium[16–18] catalysts showing the behavior of AlPO$_4$ as excellent metal supports. In this connection, aluminum phosphates have also been used as supports for platinum[19] and palladium,[20] respectively.

In the present study we investigate the nonoxidative dehydrogenation of some alkylbenzenes (R=Et, *n*-Pr, and *i*-Pr) over rhodium catalysts at 1 wt% supported on the same two AlPO$_4$ supports previously employed as nickel supports[11] which lets us compare the influences of the two metals (rhodium and nickel) since the experimental conditions of this work are also same as those previously used with supported nickel catalysts.[11]

Experimental

Catalysts. Two Rh/AlPO$_4$ catalysts (1 wt% Rh) have been used. The AlPO$_4$ supports (Al/P=1) were obtained by precipitation with ammonia (F) or propylene oxide (P). The supported rhodium catalysts (Rh/AlPO$_4$-F, Rh/AlPO$_4$-P) were prepared by impregnation to incipient wetness with aqueous rhodium chloride solution followed by oven drying (24 h, 390 K) and reduction in flowing hydrogen (200 cm^3 min^{-1}) at 473 K as has been described elsewhere.[21] Besides, metal surface area, S, was, previously, obtained[21] from volume mean diameter, d_V, determined by TEM measurements assuming a spherical geometry of the metal particles (Rh/AlPO$_4$-F: d_V=4.2 nm and S=115 m^2 g$_{Rh}^{-1}$; Rh/AlPO$_4$-P: d_V=5.4 nm and S=90 m^2 g$_{Rh}^{-1}$).

The acid-base properties of the catalysts were determined by a spectrophotometric method previously described[22,23] that allows titration of the amount of irreversibly adsorbed benzoic acid (pK_a=4.19) or pyridine (pK_a=5.25) employed as titrant agents of basic and acid sites, respectively. For rhodium catalysts and supports (Rh/AlPO$_4$-F, Rh/AlPO$_4$-P, AlPO$_4$-F, and AlPO$_4$-P) the concentration of basic sites was 156, 152, 200, and 166 mol g^{-1}, and the concentration of acid sites 165, 163, 190, and 227 mol g^{-1}, respectively.

Apparatus and Procedure. The experiments were carried out in a tubular fixed-bed reactor (15×120 mm) with a continuous flow system at atmospheric pressure. The reactor was heated by a tubular electric furnace and the prescribed temperature (693—853 K) was monitored by a thermocouple located in the reactor wall. Isothermal temperatures were measured within an accuracy of ±1 K. The top section of the reactor which functioned as a vaporizer and preheater was packed with glass beads. Fresh catalyst was used in each experiment. The standard pretreatment of the catalyst consisted in heating in a 120 cm^3 min^{-1} nitrogen (99.999%, H_2O<3 ppm) stream for 1 h at the reaction temperature.

The starting materials: ethyl- (EB), propyl- (*n*-PB), and isopropylbenzene (*i*-PB) were supplied by Merck p.a., and purified by distillation under reduced pressure and low temperature. Each substrate was fed at several rates (F in the interval 10—0.1 cm^3 min^{-1}) by means of a microfeeder (Perfusor VI B. Braun), vaporized and passed through the catalyst zone. Nitrogen was used as a carrier gas with a constant flow of 120 cm^3 min^{-1}.

The liquid products were condensed and analyzed by gas chromatography using 5% polyphenylene oxide on Chromosorb G-AW DMCS 80/100 column. Furthermore, a spectrophotometric analysis of the different samples was made due to the low conversion values obtained (<0.5%) at the higher F values. These experiments are developed at the wavelength of the maximum absorption of the dehydrogenation products in cyclohexane solutions (spectroscopic grade, Merck) and between the concentrations where the Lambert-Beer law fits.

Results and Discussion

The gas chromatographic analysis for all runs indicated that the only reaction products obtained were those corresponding to the dehydrogenation reaction of the alkylbenzenes: styrene, α-, and β-methylstyrene, respectively.

Dehydrogenation reactions were carried out under conditions where the reaction rate, R, was not influenced by diffusion. Thus, the average particle size of the catalysts used (<0.149 mm) determines that the reactions were not influenced by internal diffusion. On the other hand, the representation of R (obtained for 0.4 g of catalyst at several feed rates, F) against F, as shown in Fig. 1a, indicated the absence of external diffusion effects in the present experimental conditions for feed rates over 1.2×10^{-4} mol s^{-1}. According to these results, the bulk of the kinetic runs was performed at a fixed ratio of catalyst mass (0.4 g) and at least three feed rates in the interval 1.2—14×10^{-4} mol s^{-1}, at temperatures between 693—853 K.

In the present experimental conditions the reaction can take place in a negligible extension in the absence of the catalyst, especially at the highest temperatures. Furthermore, identical negligible activities are obtained when the different supports are used as cata-

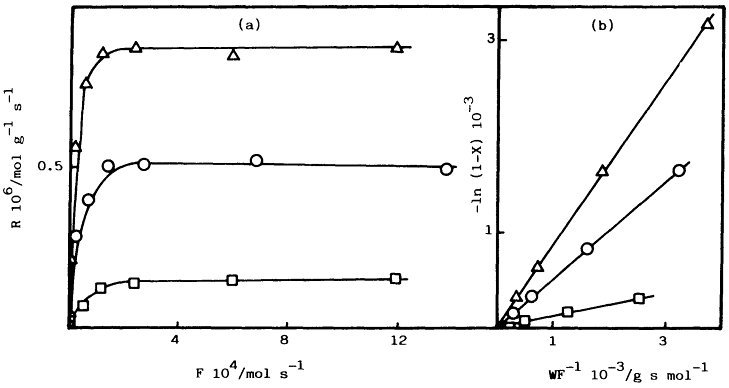

Fig. 1. (a) Dehydrogenation rate, R, of alkylbenzenes on 0.4 g of Rh/AlPO$_4$-F at 723 K as a function of feed rate, F. (b) Least-squares fit of Eq. 1 to the initial conversion data, X, at different residence time, W/F. (○) Ethylbenzene, (□) propylbenzene, (△) isopropylbenzene.

Table 1. Reaction Rate Constants, k (mol g^{-1} s^{-1}) and Specific Reaction Rates, k_S (mol s^{-1} m^{-2}$_{Rh}$) of Two Catalysts in the Dehydrogenation of Alkylbenzenes Studied at Different Temperatures

Catalyst	T	EB		n-PB		i-PB	
	K	$10^6\,k$	$10^6\,k_S$	$10^6\,k$	$10^6\,k_S$	$10^6\,k$	$10^6\,k_S$
Rh/AlPO$_4$-P	693	0.28	0.31	0.01	0.01	0.16	0.26
	723	0.49	0.55	0.02	0.02	0.45	0.50
	753	0.80	0.89	0.07	0.08	0.72	0.80
	773	1.19	1.32	0.12	0.13	1.10	1.22
	793	1.65	1.83	0.17	0.19	1.50	1.67
	823	2.25	2.50	0.32	0.36	2.37	2.64
	853	3.56	3.96	0.77	0.85	3.63	4.04
Rh/AlPO$_4$-F	693	0.32	0.28	0.07	0.06	0.49	0.50
	723	0.51	0.45	0.12	0.11	0.88	0.76
	753	0.80	0.69	0.25	0.22	1.08	0.94
	773	1.10	0.95	0.38	0.33	1.40	1.22
	793	1.28	1.12	0.45	0.39	2.11	1.83
	823	1.99	1.73	0.75	0.65	3.14	2.73
	853	2.81	2.45	1.21	1.05	4.60	4.00

lysts. Accordingly it may be assumed that the catalytic activity is exclusively developed on the rhodium metal surface, as occurs in nickel catalysts.[11]

The initial conversion data, X (<5%) (defined as the number of moles of dehydrogenated alkylbenzene per mole of alkylbenzene fed) are fitted in a first-order rate equation, Fig. 1b, at residence times lower than 4000 g s mol^{-1}.

$$\ln 1/(1-X) = k(\mathrm{W/F}) \qquad (1)$$

The slope of the straight lines yields the value of the reaction rate constant, k (in mol g^{-1} s^{-1}). In Table 1 the k and specific reaction rate constants, k_S (in mol s^{-1} m$^{-2}{}_{\mathrm{Rh}}$) values for the three alkylbenzenes with the two catalysts at each temperature are collected.

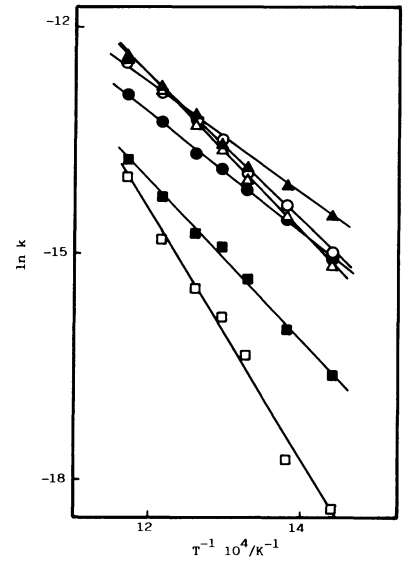

Fig. 2. Arrhenius plots for the dehydrogenation of ethylbenzene: (○) Rh/AlPO$_4$-P, (●) Rh/AlPO$_4$-F; propylbenzene: (□) Rh/AlPO$_4$-P, (■) Rh/AlPO$_4$-F; and isopropylbenzene: (△) Rh/AlPO$_4$-P, (▲) Rh/AlPO$_4$-F.

The results collected in Table 1 show that the catalytic activities of both supported rhodium catalysts are similar so that they do not exhibit a metal-support interaction effect as previously obtained with supported nickel catalysts in the same experimental conditions.[11] With respect to this, we see that specific catalytic activity of rhodium catalysts is clearly higher (between 2 and 3 times) than those obtained with nickel catalysts in the dehydrogenation of EB and *i*-PB. Such differences are not as high in *n*-PB.

The results obtained in the temperature range studied are summarized in Fig. 2 where we can see the evolution of catalytic activity with temperature which lets us apply the Arrhenius equation obtaining the corresponding values of apparent activation energies, E_a, and Arrhenius constants, $\ln A$, collected in Table 2.

Furthermore, the Eyring equation also evaluates the temperature dependence of reaction rate constants in terms of transition state theory by separating enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, components. Their corresponding values, obtained by plotting $\ln(k_S T^{-1})$ against T^{-1} are also shown in Table 2.

We can also see in Fig. 3 how the kinetic parameters $\Delta H^{\neq}$ against $\Delta S^{\neq}$ for rhodium catalysts, in Table 2, and nickel catalysts, previously obtained,[11] fit straight lines for each alkylbenzene. This enthalpy-entropy relationship may be adscribed to the existence of a linear free energy relationship (LFER):

$$\Delta G^{\neq}_{\mathrm{const}} = -\theta R \ln K^{\neq} = \Delta H^{\neq} - \theta \Delta S^{\neq} \qquad (2)$$

known as the "compensation effect" or "isokinetic relationship" (IKR)[24–26] although the most habitual representation is through the equation

$$\ln A = \ln \alpha + E_a/\theta R \qquad (3)$$

where R is the gas constant, θ the isokinetic temperature at which identical values of reaction rate constant $k=\alpha$ are obtained, $K^{\neq}$ the equilibrium

Table 2. Apparent Activation Energies, E_a (kJ mol^{-1}), Arrhenius Constants, $\ln A$ (mol s^{-1} m$^{-2}{}_{\mathrm{Rh}}$), Activation Enthalpies, $\Delta H^{\neq}$ (kJ mol^{-1}) and Activation Entropies, $\Delta S^{\neq}$ (J mol^{-1} K^{-1}) with Their Respective Standard Deviations, for the Catalysts and Substrates Studied

Substrate		Rh/AlPO$_4$-P	Rh/AlPO$_4$-F
Ethylbenzene	E_a	78.0±2.0	66.0±1.0
	$\ln A$	−1.4±0.2	−3.6±0.2
	$\Delta H^{\neq}$	71.6±2.0	60.0±1.0
	$\Delta S^{\neq}$	−274.0±2.0	−292.0±2.0
Propylbenzene	E_a	137.0±6.0	87.0±3.0
	$\ln A$	5.0±1.0	−1.4±0.4
	$\Delta H^{\neq}$	131.0±6.0	81.0±3.0
	$\Delta S^{\neq}$	−217.0±2.0	−274.0±3.0
Isopropylbenzene	E_a	84.0±1.0	64.0±4.0
	$\ln A$	−0.5±0.2	−3.5±0.7
	$\Delta H^{\neq}$	78.0±1.0	58.0±4.0
	$\Delta S^{\neq}$	−267.0±2.0	−291.0±6.0

constant of the activated complex and $\Delta G^{\neq}$ the activation free energy. Thus, the values of isokinetic parameters for each substrate (θ, $\ln \alpha$, $K^{\neq}$, and $\Delta G^{\neq}$) are obtained from slopes and intercepts in Eqs. 2 and 3 and collected in Table 3.

Furthermore, if an IKR holds for any set of reactions of the same type exhibiting the same value of $\Delta G^{\neq}$ throughout the experimental temperature range, a single common interaction mechanism can be expected.[24,27,28] In agreement with this and on the basis of the results shown in Fig. 3 and Table 3 we have to conclude that the nonoxidative gas-phase dehydrogenation of alkylbenzenes on Rh/AlPO$_4$ catalysts is carried out through the identical concerted mechanism previously described for Ni/AlPO$_4$ catalysts,[11] developed throughout the reversal of the steps of a classical Horiuti–Polanyi type noncompetitive mechanism,[29] and describing the hydrogenation of an olefinic double bond.

This concerted character can also be accounted for by consideration of the kinetic parameters presented in Table 2. Thus, the negative values of $\Delta S^{\neq}$ indicate that, on going from the ground state to the transition state, an extensive restriction in the degrees of freedom must be considered. This highly ordered transition state is consistent with a reaction mechanism whose slowest step is the stabilization and immobilization of reactant molecules on catalyst active sites. With respect to this, the reaction rate is proportional to the quantity of adsorbed reactant molecules, and the reverse reaction is negligible. Besides, the relatively low $\Delta H^{\neq}$ values appear to be consistent with a concerted evolution in the limiting adsorption step which also must be associated with the low values $\Delta S^{\neq}$.

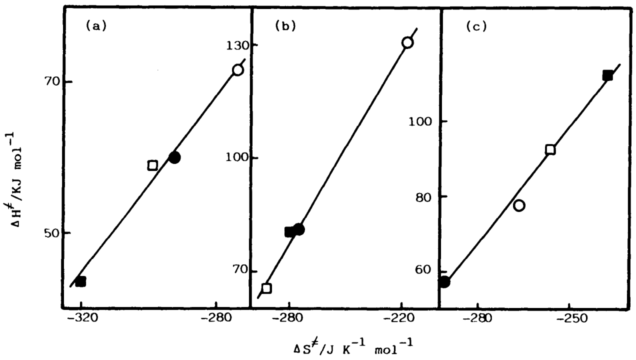

Fig. 3. Compensation effect between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for (a) ethylbenzene, (b) propylbenzene, and (c) isopropylbenzene with different catalysts: (○) Rh/AlPO$_4$-P; (●) Rh/AlPO$_4$-F; (□) Ni/AlPO$_4$-P; and (■) Ni/AlPO$_4$-F.

In the present mechanism, the active sites on the metal surface are looked on as surface complexes[29–32] with three degrees of coordinative unsaturation where it is possible to absorb two hydrogens and an olefin at the same time in the transition state. The transfer of the two hydrogen atoms from the alkylbenzenes throughout a concerted process, where the interaction with the catalyst removes the symmetry restrictions imposed by the Woodward–Hoffmann rules, leads directly to the olefinic double bond and a hydrogen molecule formation.[33] In agreement with this, Wang et al.[3,34] described the nonoxidative dehydrogenation of ethylbenzene over TiO$_2$–ZrO$_2$ catalysts through a concerted two center mechanism, where zirconium ions act like Lewis acid, and titanium ion as a base.

On the other hand, the reaction rate is only determined by the number of active sites present in the reaction. This number is determined not only by the metal surface area (related to the catalyst weight and metal dispersion) but also to the density of active sites on the metal surface, which is closely associated to the metal-support interaction effects. In this way, the higher catalytic activity of Rh/AlPO$_4$ with respect to Ni/AlPO$_4$ catalysts ought to be related to their different behavior in relation to the metal-support interaction effects. Thus, while in supported nickel catalysts the metal deposition induced a strong decrease in the number of acid sites while the number of basic sites remained almost unchanged,[11] in the Rh/AlPO$_4$ catalyst, according to the present results, the metal deposition practically does not induce appreciable changes in either the number of acid sites or basic ones. However, the potential effect of the different metal content ought to be also considered in order to explain this differential behavior between Ni and Rh supported catalysts.

According to Bartholomew et al.[35,36] such metal-support interaction can be attributed to a transfer of electrons between the nickel atoms and the acid sites on the support surface. Possibly due to the higher reduction potential in rhodium atoms, such electron transfer is not developed in Rh/AlPO$_4$ catalysts thus obtaining an enhanced catalytic activity with respect to Ni/AlPO$_4$ catalysts, as also obtained habitually in liquid-phase catalytic hydrogenation of the olefinic double bond.[13,16,17,37] So, here we have an interesting

Table 3. Values of $\ln \alpha$ and θ^{a} (K) Obtained from the Representation of $\ln A$ againt E_a and Values of θ^{b} (K), $\Delta G^{\neq}$ (kJ mol^{-1}), and $\ln K^{\neq}$ Obtained from the Representation of $\Delta H^{\neq}$ againt $\Delta S^{\neq}$, Corresponding to Substrates

Substrate	$\ln \alpha$	θ^{a}	θ^{b}	$\Delta G^{\neq}_{\mathrm{const}}$	$\ln K^{\neq}$
Ethylbenzene	−17.0±1.0	613±67	596±65	235±19	−47±6
Propylbenzene	−13.7±0.6	870±40	867±40	319±11	−44±3
Isopropylbenzene	−10.7±0.8	1038±74	1028±74	355±19	−42±4

difference between the catalytic behavior of Rh and Ni supported catalysts: The former does not exhibit important metal-support interaction effects which could explain in part its excellent catalytic activity. In spite of this, it has not been studied extensively to date as evidenced by the absence of publications during the last few years.

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, Spain. The authors also acknowledge the grammatical revision of the manuscript carried out by Prof. M. Sullivan.

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