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Hydrogen Spillover Effects in the Hydrogenation of Benzene over $Pt/\gamma\text{-}Al_2O_3$ Catalysts

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A study has been made of the presence of hydrogen spillover on $Pt/\gamma\text{-}Al_2O_3$ catalysts and its influence on the hydrogenation of benzene to cyclohexane. The specific activity, referred to Pt metal, increases with the degree of dilution of the catalyst with the $\gamma\text{-}Al_2O_3$ support up to 50/1 and remains almost constant in more diluted systems; this indicates that atomic hydrogen does not migrate beyond a certain distance, depending on the granulation and texture of the solid mixture. The results suggest that hydrogenation occurs both on the $Pt/\gamma\text{-}Al_2O_3$ and on the diluent $\gamma\text{-}Al_2O_3$. The ratio between the specific conversion of diluted and undiluted catalysts is temperature independent and the Arrhenius plots for various (un)diluted catalysts all show an equal apparent activation energy value of 9.16 kcal/mol. A hypothesis for the hydrogenation mechanism of benzene over the $\gamma\text{-}Al_2O_3$ diluent is reported.

INTRODUCTION

Recently considerable interest has been shown in the endothermic dehydrogenation process of cyclohexane as a means of accumulating thermal energy and transferring reaction products over a distance (chemical heat pipe) (*1*). This stems from various favourable characteristics of the reaction, such as its high thermal effect, the wide commercial availability of the reagents at low cost, and the ease of storing the products. The reaction occurs almost quantitatively between 250 and 350°C and is therefore suitable for accumulating off-peak heat from thermoelectric power stations, and storing heat from nuclear and solar stations.

The reverse process, namely, the exothermic hydrogenation of benzene (49.2 kcal/mol C_6H_{12}), has been widely reported in the literature and is industrially applicable. Adaptation to accumulation problems requires the development of catalysts that are active in the gas-phase reaction at high temperatures ($T \geq 250°C$) and stable with time, so that a greater thermodynamic efficiency is obtained in the utilization of the heat evolved from the reaction.

With the purpose of considering possible solutions to the problem, we have studied the catalytic activity of $Pt/\gamma\text{-}Al_2O_3$ catalysts diluted with different quantities of the support. In this context it should be mentioned that the diluted-bed theory has been studied in recent years especially to achieve control of the temperature and conversion profiles for such highly exothermic reactions (mainly oxidations) (*2*).

In the case of catalytic hydrogenation some authors have drawn attention to the role of spillover on the reaction mechanism (*3–9*). The phenomenon consists of dissociative adsorption of hydrogen on the metal and migration of the atomic hydrogen to the surface of the support. The support is then able to activate reactions (e.g., hydrogenation, isomerization) which in the absence of the metal it could not otherwise achieve.

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For example, various metal oxides (e.g., WO_3, MoO_3, CrO_3) are reduced with hydrogen even at room temperature if they are doped with Pt or are placed in contact with platinum black or Pt/Al_2O_3(SiO_2) (*10–14*). The phenomenon also involves granules adjacent to those supporting the metal; in this way alumina and silica are rendered active in the hydrogenation reaction after having been in contact with a catalyst (Pt, Ni/support) which has been able to transfer atomic hydrogen to them by spillover (*3*). Carter *et al.* (*9*) reported the spillover phenomenon of hydrogen on Pt/SiO_2 (0.5% wt Pt) diluted with SiO_2 or Al_2O_3 in the hydrogenation of ethylene; the reaction rate for the catalyst diluted with Al_2O_3 was greater than that in the case of SiO_2. Kramer (*15*) identifies spillover hydrogen by means of thermal desorption by comparison with a metal-free support exposed to atomic hydrogen before desorption. In particular the surface diffusion of atomic hydrogen on alumina has been studied using temperature-programmed desorption and the rate and amount of spillover hydrogen were calculated quantitatively as a function of the adsorption pressure, temperature, and time, and the diffusion and adsorption parameters of the atomic hydrogen (surface diffusion coefficient, activation energy for the surface diffusion, and surface capacity of the alumina for the atomic hydrogen) were evaluated (*16*). Reactive hydrogen diffusion has also been studied following the reduction of a thin film of Ag_2S in contact with a Pt film or separated from the platinum by means of carbon or SiO_2 (*17*).

Sancier (*18*) has studied the hydrogenation of benzene in a slug reactor at T = 150°C using Pd/Al_2O_3 catalyst (2.2% wt Pd) diluted with alumina; he found a great increase in catalytic activity (per mg of palladium) when the dilution was increased up to a performance factor of about 3 for a dilution of 200 to 1. With a view to modifying the activity level required for the above-mentioned purposes, we have verified the presence of spillover in benzene hydrogenation on γ-Al_2O_3-supported platinum catalysts with variation of the metal content and degree of dilution.

EXPERIMENTAL

Equipment and Procedure

The benzene hydrogenation reaction was carried out continuously in an isothermal microreactor connected to a gas-chromatographic unit.

After passing through a Deoxo purifier (filled with Cu filings and kept at 300°C) and a molecular sieve dehydrator, the H_2 flow (50 cm^3/min) entered a saturator kept in a thermostat regulated at 30°C to achieve a hydrogen/benzene ratio of 5.33, used throughout all our experiments. The reacting mixture then passed through a Pyrex glass reactor (1 = 12.5 cm; ϕ_i = 1.7 cm) heated by a tubular oven thermoregulated to ±1°C. The reaction temperature was taken as the mean between the external temperature at the reactor and the internal temperature measured by a Cr–Al thermocouple housed in a glass tube (ϕ_e = 0.6 cm) inside the reactor.

The reaction products were analyzed by a Carlo Erba Model C Fractovap with a chromatographic column (1 = 1.5 m; ϕ_i = 4 mm) containing UC 550 at 25% on Chromosorb P and kept at 85°C. Since cyclohexane and benzene were the only organic components of the reaction mixture, the benzene conversions were calculated from the ratio between the corrected area of the benzene peak and the total corrected area of the benzene and cyclohexane peaks.

Reagents and Catalysts

Commercially available hydrogen (SiO product, PP type) was used. Benzene ("Baker Analyzed Reagent" thiophene free) had a 99% purity. The γ-alumina (S.A. = 288 m^2/g) was supplied by Pechiney St. Gobain with a 16- to 30-mesh granulometry.

Pt/γ-alumina catalysts with 0.31% wt Pt (catalyst A_1) and 1.35% wt Pt (catalyst A_4) were prepared by impregnating γ-alumina with aqueous solutions of H_6PtCl_6 and continuous stirring for 30 min at room temperature. After filtration, the solid was dried at 110°C for 24 h. The metal surface area, measured from CO adsorption at room temperature and atmospheric pressure, assuming a CO : Pt ratio of 1 : 1, was found to be 0.19 and 0.81 m^2 Pt/g catalyst for catalysts A_1 and A_4, respectively.

The Pt/γ-Al_2O_3 catalysts were diluted with γ-Al_2O_3 by mixing at volume ratios of 1/3, 1/9, 1/20, 1/50, and 1/100. Before the reaction the catalysts were activated under a hydrogen flow at 500°C for 3 h. As the catalytic bed volume (catalyst + diluent) was kept constant for all dilutions, the contact time referred to the total solid was constant.

RESULTS

The thermodynamic conversions of benzene to cyclohexane for $p_{H_2}/p_{C_6H_6} = 5.33$ and $P = 1$ atm are 100% up to 200°C, and decrease at higher temperatures.

Figures 1 and 2 show the benzene conversions as a function of the temperature at various levels of dilution of catalysts A_1 and A_4 with γ-Al_2O_3. All conversion curves show a maximum between 150 and 190°C. The curve pattern reflects a positive influence of the reaction kinetics at lower temperatures, whereas at higher temperatures the thermodynamic effect of the reaction prevails and so the conversions decrease. In addition, the maxima shift towards higher temperatures with increasing dilution of the catalyst. The experiments bear out that whereas the total conversions decrease with an increase of dilution level, the conversions referred to the weight unit (mg) of Pt or the specific activity of the reaction (mol C_6H_6 converted/h mg Pt) increase. This is shown in Tables 1 and 2 for catalysts A_1 and A_4 at 100 and 110°C, respectively, and indicate a marked increase in the specific activity of benzene hydrogenation to cyclohexane over Pt/γ-Al_2O_3 catalysts as a result of dilu-

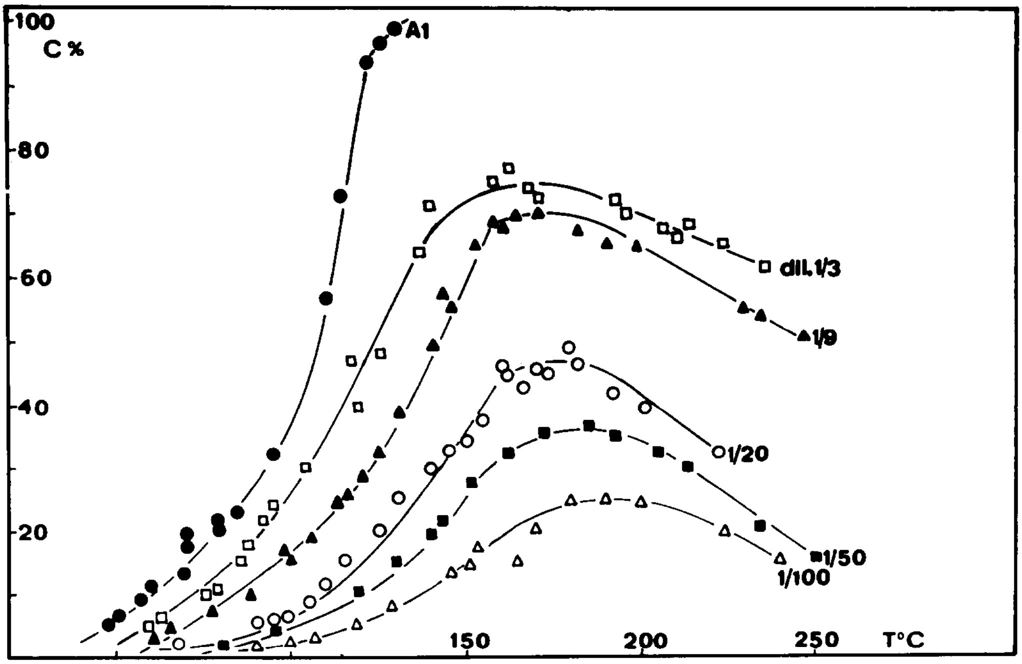

FIG. 1. Influence of reaction temperature on conversion of benzene over A_1 catalysts (0.31% wt Pt on γ-Al_2O_3) at various levels of dilution (1/3, 1/9, 1/20, 1/50, and 1/100) with γ-Al_2O_3. $W/F = 2.13 \times 10^6$ g sec/mol.

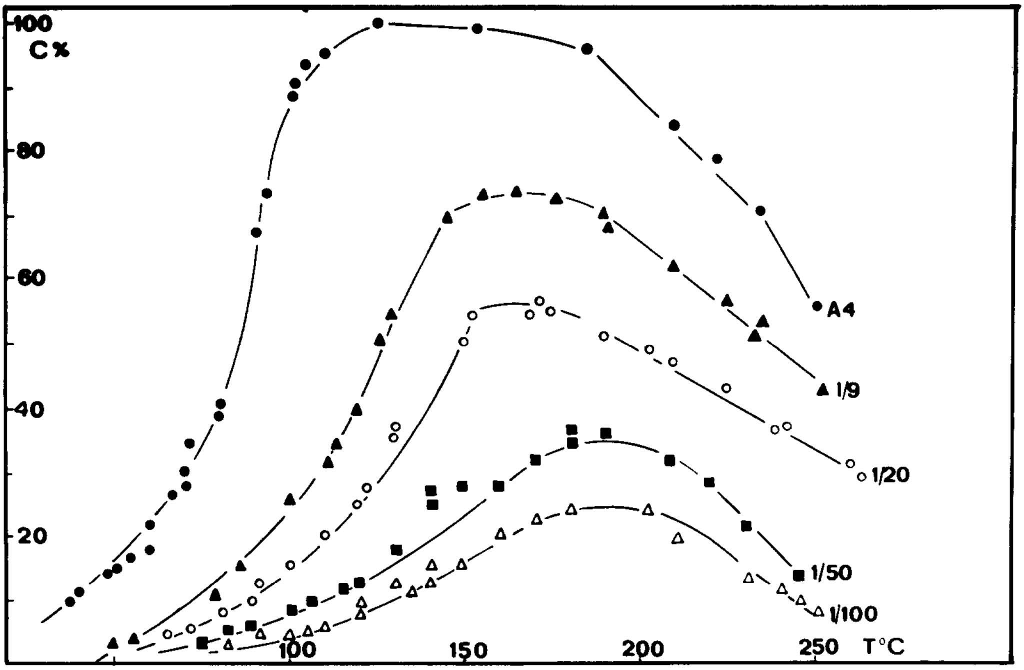

FIG. 2. Influence of reaction temperature on conversion of benzene over A_4 catalysts (1.35% wt Pt on γ-Al_2O_3) at various levels of dilution (1/9, 1/20, 1/50, and 1/100) with γ-Al_2O_3. $W/F = 0.73 \times 10^6$ g sec/mol.

tion with γ-Al_2O_3. The results suggest that a part of the hydrogenation occurs on the Pt/γ-alumina catalyst and the rest on the diluent γ-Al_2O_3. It should be noted that the activity of alumina on its own is negligible; at 138°C the benzene conversion is only 0.4%.

In our experiments the contact time, expressed as W/F (g sec mol^{-1}), has been chosen so as to have conversion levels which bring out better the differences between the mixtures (catalyst + diluent support) considered. With catalyst A_1, which contains a smaller quantity of Pt (0.31%) compared with A_4 (Pt = 1.35%), W/F (2.13×10^6 g sec mol^{-1}) is higher than the one used for the other catalyst ($W/F = 0.73 \times 10^6$ g sec mol^{-1}).

TABLE 1

A_1 Catalysts (0.31% wt Pt on γ-Al_2O_3) Variously Diluted with γ-Al_2O_3

Catalyst (g)		$\frac{\gamma\text{-}Al_2O_3}{\text{Catalyst } A_1}$	mg Pt	Percentage conversion		$\frac{\text{mol } C_6H_6 \text{ converted}}{\text{h} \times \text{mg Pt}} \times 10^3$
Catalyst A_1	γ-Al_2O_3			C% total	C% × mg Pt	
2.11	0	0	6.54	40.0	6.12	0.218
0.53	1.58	3:1	1.64	26.5	16.06	0.577
0.211	1.82	9:1	0.65	15.0	22.93	0.819
0.100	2.01	20:1	0.31	8.0	25.64	0.916
0.042	2.07	50:1	0.13	5.0	38.40	1.371
0.021	2.09	100:1	0.06	2.5	39.00	1.392

Note. H_2/benzene = 5.33; $F_{C_6H_6} = 3.57 \times 10^{-3}$ mol/h; $W/F = 2.13 \times 10^6$ g sec/mol; $T = 100°C$.

TABLE 2

A_4 Catalysts (1.35% wt Pt on γ-Al_2O_3) Variously Diluted with γ-Al_2O_3

Catalyst (g)		γ-Al_2O_3 / Catalyst A_4	mg Pt	Percentage conversion		$\frac{\text{mol } C_6H_6 \text{ converted}}{\text{h} \times \text{mg Pt}} \times 10^3$
Catalyst A_4	γ-Al_2O_3			C% total	C% × mg Pt	
0.720	0	0	9.72	96.0	9.88	0.353
0.072	0.648	9:1	0.97	32.5	33.51	1.197
0.0343	0.686	20:1	0.46	20.0	43.19	1.542
0.0141	0.707	50:1	0.19	11.0	57.80	2.064
0.0072	0.713	99:1	0.097	6.0	61.7	2.203

Note. H_2/benzene = 5.33; $F_{C_6H_6} = 3.57 \times 10^{-3}$ mol/h; $W/F = 0.73 \times 10^6$ g sec/mol; T = 110°C.

Figures 3 and 4 report the conversion of benzene as a function of the value of W/F for the catalysts diluted at the 20/1 level (γ-Al_2O_3/A_1 and γ-Al_2O_3/A_4) and show that the catalytic activity is almost linear with W/F at least up to the values adopted (2.13×10^6 and 0.73×10^6 g sec mol^{-1} for A_1 and A_4, respectively) and at the lower temperature; in addition, under our conditions the phenomena of mass transfer or of external diffusion are completely absent.

Figure 5 compares the effect of temperature on the specific activity ratio R on the diluted and undiluted A_4 catalyst; R varies from 2.5 to 5 for dilutions of 9/1 to 100/1 and is practically independent of the reaction temperature between 60 and 110°C. For higher temperatures the ratio considerably increases since the effect of the temperature on the conversion decreases considerably in the case of the undiluted catalyst (values close to equilibrium ones).

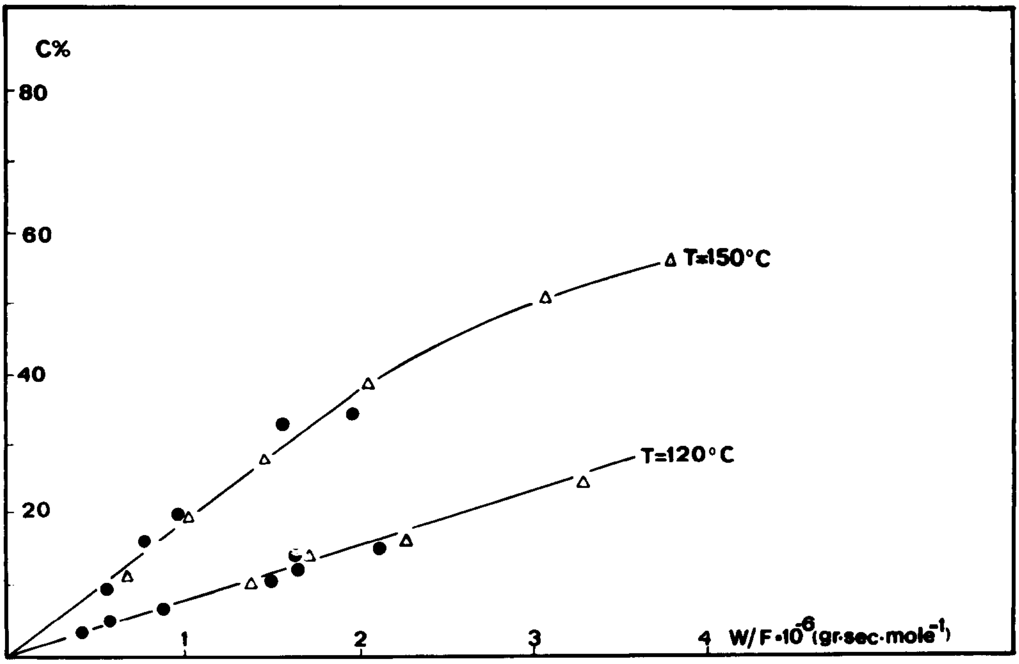

FIG. 3. Conversion of benzene to cyclohexane over γ-Al_2O_3/A_1 (dild 20/1) as a function of W/F (g sec/mol). (●) W = 2.11 g; (△) W = 4.22 g.

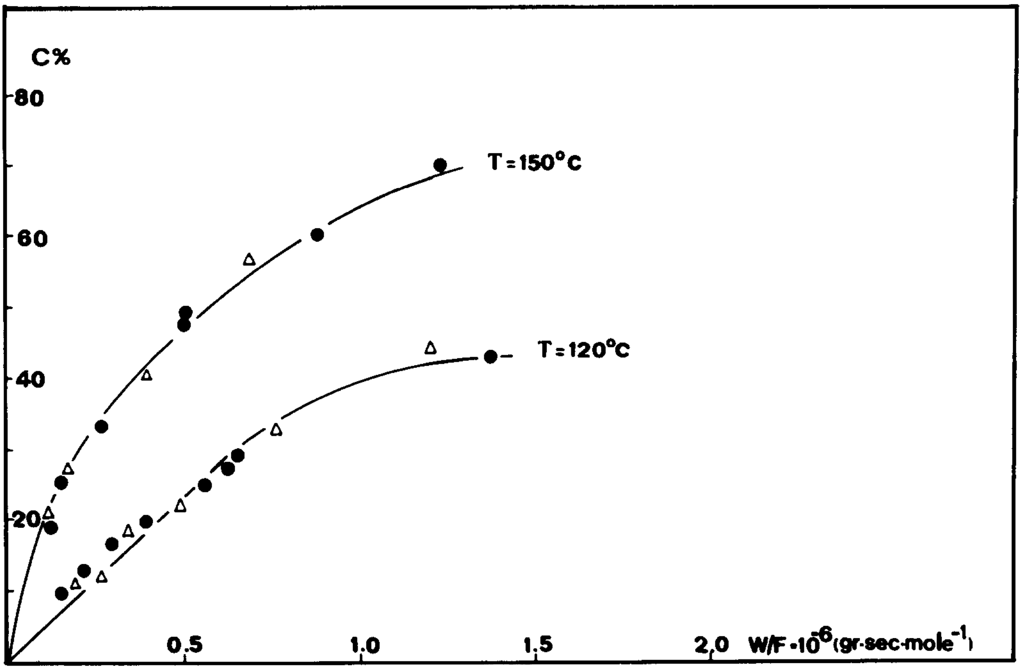

FIG. 4. Conversion of benzene to cyclohexane over γ-Al_2O_3/A_4 (dild 20/1) as a function of W/F (g sec/mol). (●) $W = 0.72$ g; (△) $W = 1.44$ g.

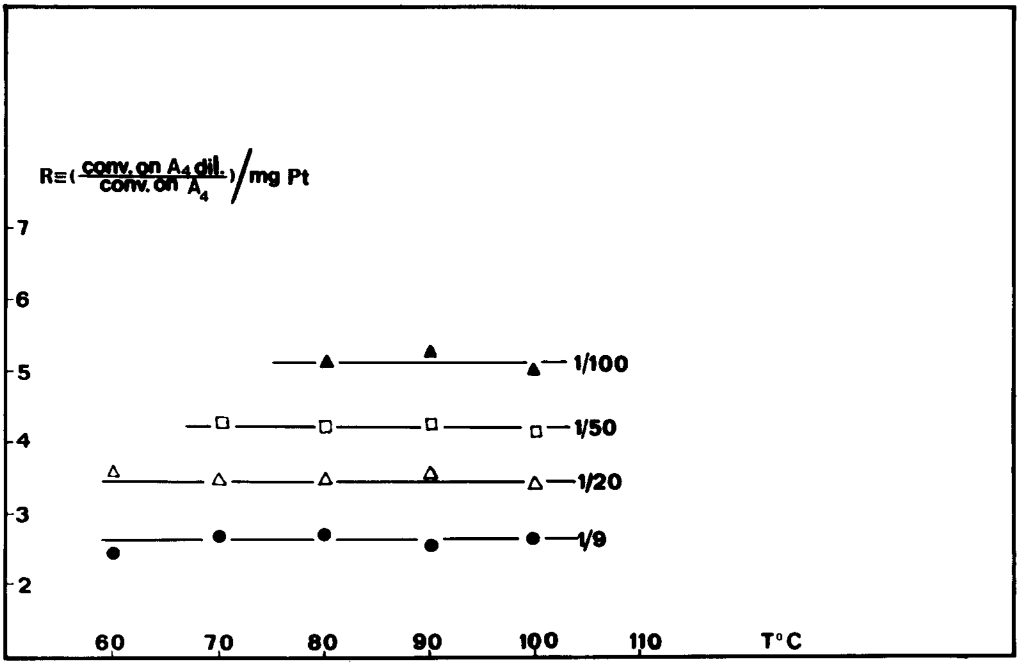

FIG. 5. Specific activity ratio (diluted and undiluted A_4) vs temperatures at various levels of dilution. $W/F = 0.73 \times 10^6$ g sec/mol.

Similar trends were observed for catalyst A_1.

DISCUSSION

According to Basset *et al.* (*19*) the hydrogenation of benzene to cyclohexane on a Pt/Al_2O_3 catalyst is a "facile" reaction in so far as the activity does not depend on the method of preparation, the platinum dispersion, the diameter distribution of the crystallites, the alumina surface area, or the chlorine content; it depends only on the platinum surface sites (Pt_s). On this basis, the turnover number (moles C_6H_6 converted per metallic site) was constant for the A_1 and A_4 catalysts that we examined, in spite of their different platinum contents. Furthermore, the reaction, which is zero order with respect to benzene, involves hydrogen and benzene adsorbed on adjacent platinum sites; benzene interacts with one such platinum site forming a π complex, whereas the molecular hydrogen is dissociatively adsorbed to form atomic hydrogen on adjacent sites.

Only Bianchi *et al.* (*3*) mention the hydrogenation of benzene on Pt/Al_2O_3 and the presence of spillover; in particular, they find that on SiO_2 activated by Pt/Al_2O_3 the reaction occurs between benzene and spillover atomic hydrogen to give cyclohexane, whereas the presence of molecular hydrogen gives rise to ethane.

The results reported above show that the presence of diluent γ-Al_2O_3, which on its own is inactive, greatly influences the specific activity of the Pt/Al_2O_3 catalyst in the hydrogenation of benzene to cyclohexane. The increase of the specific activity of the catalyst with higher degrees of dilution can be understood if one accepts that the reaction also involves the alumina diluent granules (as a result of spillover hydrogen) in addition to occurring on the sites of the Pt/γ-Al_2O_3 particles. Accordingly, we suppose that a part of the reaction occurs by means of a mechanism that involves the benzene and hydrogen adsorbed on the platinum, as was proposed by Basset *et al.* (*19*), and that another part occurs on the support as a result of some atomic hydrogen migrating from the metal to the support surface and the nearby alumina granules to react there with benzene (adsorbed on γ-alumina or gaseous), thereby increasing the specific activity of the diluted catalyst even at rather low temperature (60°C).

It follows from Tables 1 and 2 that the specific activity as a function of the degree of dilution increases up to a dilution of 50/1 and remains almost constant in more diluted systems. Since the total surface area, per gram of catalyst and diluent, can be considered constant at any degree of dilution, the distance between the surface metal atoms assumes an important role in determining the specific activity. As the platinum crystallites or atoms are uniformly distributed over the entire surface of the undiluted catalyst there is a high probability of collision between spillover $H^{\cdot}$ atoms and thus of formation of molecular hydrogen, which is inactive in benzene hydrogenation. Dilution achieves separation of the single granules covered by platinum and a higher degree of dilution decreases the collision rate. This means greater stability and an increase in spillover atomic hydrogen and specific activity. This pattern appears to be valid at least until a dilution of 50/1, after which further dilution brings no benefit. This stands in relation to the fact that atomic hydrogen cannot migrate beyond certain distances, depending on the grain size and texture of the solid mixture. Migration of atomic hydrogen has been reported to occur over distances of about 2000 Å. For palladium/alumina diluted with alumina Sancier (*18*) found values ranging from 500 to 20,000 Å. However, it is obvious that there must be a point where the additional surface area of the diluent brings no further benefit to the reaction.

Figure 6 reports conversions as a function of the platinum percentage (quantity of metal referred to the total weight of the catalytic bed) at $T = 100°C$ and $W/F = 0.59 \times 10^6$ g sec mol^{-1}. The conversions vary

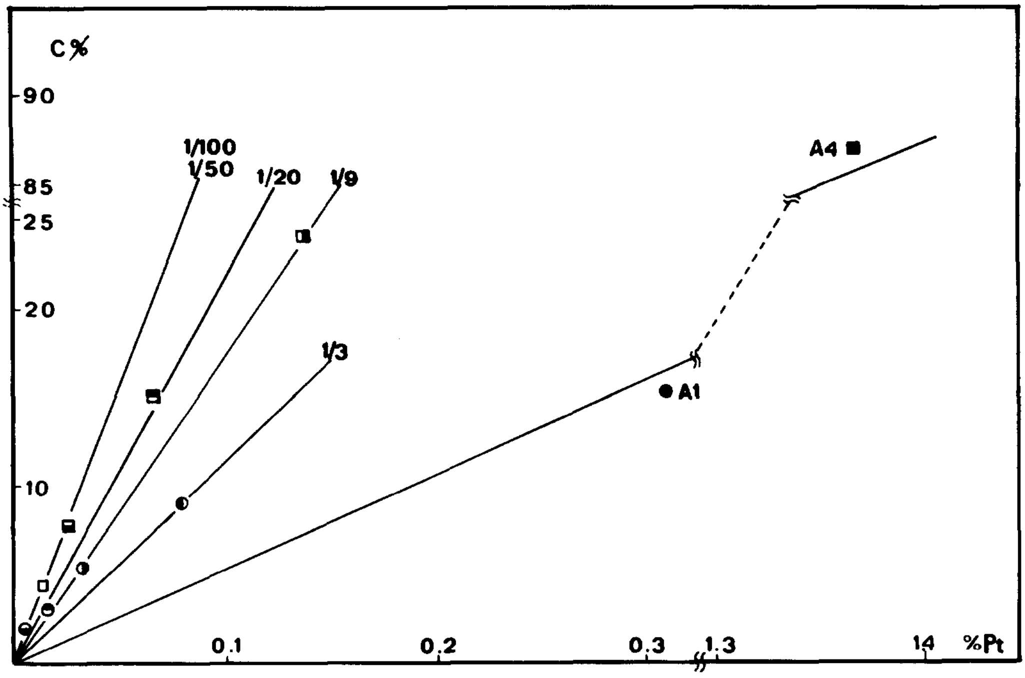

FIG. 6. Conversion of A_1 and A_4 catalysts diluted with γ-Al_2O_3 as a function of the platinum content. $T = 100°C$; $W/F = 0.59 \times 10^6$ g sec/mol. (●, ⊖, ◓, ◑, ◐) A_1 and A_1 diluted at 1/50–1/100, 1/20, 1/9, and 1/3, respectively. (■, □, ⊟, ⊞, ◨) A_4 and A_4 diluted at 1/100, 1/50, 1/20, and 1/9, respectively.

linearly with the platinum content for all degrees of dilution of the catalysts. This is not unexpected in that A_1 and A_4 have a very similar metallic specific surface area (166.7 and 163.2 m^2/mg Pt, respectively) and hence the same turnover number. The slope of the curves gradually increases with the degree of dilution. For dilutions exceeding 50/1 the curves coincide.

The pattern of Fig. 6 is yet further proof of the fact that dilution increases the specific activity. In fact, considering the points relative to a given platinum percentage, the conversions are proportionally greater with the degree of dilution. Such catalysts have the same platinum percentage, the same number of metallic sites, and the same total surface area, while the difference consists in the fact that the platinum is differently arranged on the catalytic bed. Thus, in the undiluted catalyst the metal is homogeneously distributed on the support; after dilution with γ-Al_2O_3 a surface without Pt atoms (diluent granules) is mixed with catalyst particles with a Pt/granule concentration which is proportionally higher with the degree of dilution. The increase in activity is then undoubtedly to be attributed to the greater distance of these metal "concentrations" (catalyst A_1 and A_4 granules). Since atomic hydrogen is generated only on the platinum atoms, its migration on the diluent surface has to be assumed in order to explain the catalytic activity data. It is on the distance of the individual granules of catalysts A_1 and A_4 that the spillover hydrogen concentration available for the reaction of the benzene with the alumina depends.

At constant dilution, the points on the lines of Fig. 6 refer to Pt-containing granules at equal distances one from another but with a varying concentration of Pt/granule or percentage of platinum per unit of catalytic bed. The linear increase of the conversion with the Pt content indicates that the spillover level remains constant and depends only on the available diluent surface; the higher activity can be ascribed to the greater amount of metal present and therefore to the reaction on the platinum atoms according to the mechanism of Basset *et al.* (*19*). Another conclusion which can be drawn from the straight line pattern of the data at constant dilution is that formation of cyclohexane owing to hydrogen spillover on the A_1 and A_4 granules is completely insignificant compared with the reaction occurring on the metal and on the diluent surface.

On the basis of the linear variation of the conversion over a wide W/F interval (Figs. 3 and 4), Arrhenius plots have been derived between 70 and 120°C (Fig. 7). The results for various (un)diluted catalysts all show an equal slope and an apparent activation energy value of 9.16 kcal/mol. This value is very close to that reported by Basset *et al.* (*19*) for the same reaction on Pt/Al_2O_3 at $T = 50°C$ and $p_{C_6H_6} = 56$ Torr, the kinetics of which are controlled by the reaction on Pt between activated benzene and hydrogen. The increase of reaction rate with the degree of dilution is to be attributed to a greater $H^\cdot$ concentration (spillover hydrogen) and therefore to an intense reaction on the alumina surface; the benzene hydrogenation kinetics only depend on the hydrogen concentration. In addition, as the calculated surface diffusion energy of atomic hydrogen on alumina of 28–29 kcal/mol (*16*) greatly exceeds the present experimentally found value, the transformation reaction on the diluent granules is not controlled by surface diffusion of atomic hydrogen. As a result, the reaction mechanism on alumina is the same as that occurring on platinum. It is then reasonable to suppose that the slowest stage on the diluent surface is the reaction between adsorbed or gaseous benzene and spillover atomic hydrogen. This is also a direct consequence of the fact that the reaction which involves spillover hydrogen increases with dilution. If the opposite were true, benzene would react very quickly with hydrogen migrating on the surface, without giving it the chance to utilize

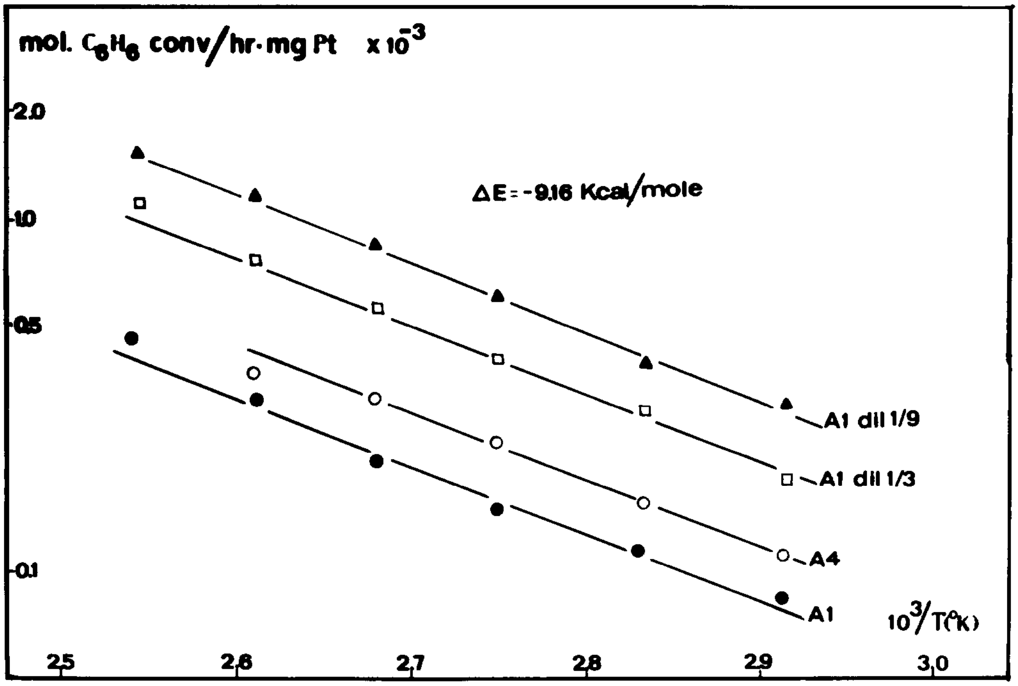

FIG. 7. Arrhenius plots of specific reaction rates. $W/F = 2.13 \times 10^6$ g sec/mol for undiluted and diluted A_1 catalysts; $W/F = 0.73 \times 10^6$ g sec/mol for A_4 catalysts.

the larger surfaces available with greater dilution.

It can also easily be understood why the ratios between specific conversions of diluted and undiluted catalysts are temperature independent (Fig. 5). In fact, as the transformation on a diluted catalyst is the sum of those occurring on platinum and alumina, it follows, in case of the same reaction mechanism, that

$$v_1 = k_1 p_{H_2}{}^{\alpha} = A_1 e^{-\Delta E/RT} p_{H_2}{}^{\alpha}$$

for catalyst A_4 and

$$v = v_1 + v_2 = k_1 p_{H_2}{}^{\alpha} + k_2 p_{H_2}{}^{\beta} = (A_1 p_{H_2}{}^{\alpha} + A_2 p_{H_2}{}^{\beta}) e^{-\Delta E/RT}$$

for catalyst A_4 + diluent. Consequently

$$\frac{v}{v_1} = \frac{(A_1 p_{H_2}{}^{\alpha} + A_2 p_{H_2}{}^{\beta})}{A_1 p_{H_2}{}^{\alpha}}$$

is temperature independent.

In conclusion, under our conditions the hydrogenation reaction of benzene (Bz) to cyclohexane (Cycl) can schematically be represented as shown in Fig. 8 and in the following series of events:

$$H_{2(g)} \overset{Pt}{\rightleftarrows} H_{2(ad)} \overset{Pt}{\rightleftarrows} 2H^{\cdot}_{(g)}, \qquad (1)$$

$$Bz_{(g)} \overset{Pt}{\rightleftarrows} Bz_{(ad)} \overset{Pt}{\rightleftarrows} \overset{*}{Bz}_{(ad)}, \qquad (2)$$

$$\overset{*}{Bz}_{(ad)} + 6H^{\cdot}_{(ad)} \overset{Pt}{\rightleftarrows} Cycl_{(ad)} \leftrightarrows Cycl_{(g)}, \qquad (3)$$

$$6H^{\cdot} \overset{\gamma\text{-}Al_2O_3}{\rightleftarrows} 6H^{+} + 6e^{-}, \qquad (4)$$

$$Bz_{(g)} \overset{\gamma\text{-}Al_2O_3}{\rightleftarrows} Bz_{(ad)}, \qquad (5)$$

$$6H^{\cdot} + Bz_{(ad)} \overset{\gamma\text{-}Al_2O_3}{\rightleftarrows} Cycl_{(ad)} \rightleftarrows Cycl_{(g)}, \qquad (6)$$

$$6H^{\cdot} + Bz_{(g)} \overset{\gamma\text{-}Al_2O_3}{\rightleftarrows} Cycl_{(g)}, \qquad (7)$$

$$2H^{\cdot} \underset{Pt}{\overset{\gamma\text{-}Al_2O_3}{\rightleftarrows}} H_2. \qquad (8)$$

Stage (4) refers to the fact that $H^{\cdot}$ is captured on alumina sites which can be surface defects, ionic vacancies, exposed trigonal aluminum, as well as impurities (*20, 21*); however, it is atomic hydrogen which reacts with benzene to give cyclohexane.

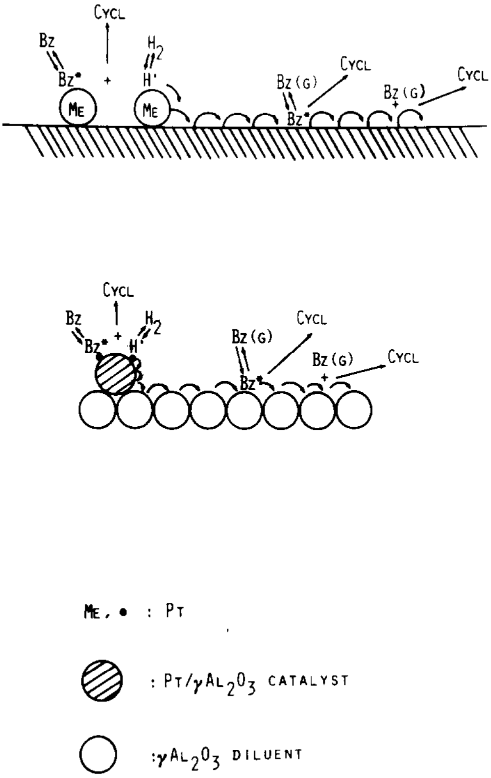

FIG. 8. Scheme of hydrogen spillover.

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