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Direct Observation of Hydrogen Spillover on Carbon-Supported Platinum and Its Influence on the Hydrogenation of Benzene[1]

S. T. Srinivas and P. Kanta Rao[2]

Catalysis Section, Physical & Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

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A study on the presence of hydrogen spillover on carbon-supported platinum catalysts was conducted. CO and H_2 uptakes were determined at ambient temperature on Pt/C catalyst variously diluted with carbon. The effect of H_2 spillover on benzene hydrogenation over Pt/C and diluted Pt/C was studied. From chemisorption results a direct observation of hydrogen spillover at room temperature was made. Activity data suggest that benzene hydrogenation occurs both on Pt/C and carbon diluent due to hydrogen spillover. The specific activity increased to a dilution level beyond which it became constant. This fact was further confirmed by H_2 uptake measurements. Arrhenius plots of various diluted samples show an equal slope resulting in a uniform value for activation energy. The mechanism of benzene hydrogenation due to spilled over hydrogen on Pt/C appears to be same as on Pt/γ-Al_2O_3. © 1994 Academic Press, Inc.

INTRODUCTION

In recent years a number of studies have been devoted to the phenomenon of "spillover," which is defined as the dissociative chemisorption or adsorption of hydrogen on the metal and the migration of atomic hydrogen to the surface of the support such as alumina, silica, carbon, etc. The reality of spillover in the sense of the migration of a species such as hydrogen from one phase where it is formed, to the support or another admixed phase, is no longer questioned. Comprehensive reviews have been published concerning mainly the description and analysis of the spillover and its probable mechanisms (1–4).

In the case of carbon H_2 spillover was observed at 350°C and the phenomenon was studied in considerable detail on platinum supported on Spheron-6 (BET SA 100 m^2/g) (5, 6); it was reported that, in the case of Pt/C, it is the contamination of the platinum surface by carbon which plays a decisive role in providing bridges for hydrogen atoms to be transported away from platinum to the carbon support itself. The necessity for such bridges may be a general requirement for the occurrence of spillover. This paper shall describe plausible explanations regarding the occurrence of hydrogen spillover and its chemistry in the carbon-supported platinum system. This system was chosen because of its great technological importance in hydrogenation reactions (7) and to make catalytic electrodes for phosphoric acid fuel cells (PAFC) for power generation (8–10).

In the supported metal catalysts attention has been focused on the role of spillover in the reaction mechanism of catalytic hydrogenation (11–16). Because of spillover hydrogen from metal site, the support will become able to activate the reactions, which in the absence of the metal would not otherwise be possible. Carter (16) reported the spillover of hydrogen on Pt/SiO_2 diluted with SiO_2 or Al_2O_3 in the hydrogenation of ethylene. It was observed that the reaction rate for catalyst diluted with Al_2O_3 was greater than that in the case of SiO_2. Sancier (17) has studied the hydrogenation of benzene in a slug reactor at 150°C using 2.2% Pd/Al_2O_3 diluted with alumina. He found that the catalytic activity increased markedly (per mg of Pd) when the dilution was increased to a performance factor of about 3 for a dilution of 200 to 1. Antonucci *et al.* (18) also found a great increase in catalytic activity towards benzene hydrogenation on Pt/γ-Al_2O_3 due to hydrogen spillover. The activity increased with respect to platinum content in the sample when it was diluted with γ-Al_2O_3. Ceckiewicz and Delmon (19) demonstrated the reaction of spilt over hydrogen for the hydrogenation of benzene; when the 0.6% Pt/γ-Al_2O_3 was mechanically diluted with alumina support in the ratio 1 : 20 the specific activity of the catalyst increased fourfold. We have undertaken this study with a view to find a direct evidence of hydrogen spillover at room temperature, and benzene hydrogenation was selected as a test reaction to verify the influence of the degree of carbon dilution on 5 wt.% Pt/C catalyst.

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[2] To whom correspondence should be addressed.

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EXPERIMENTAL

Materials

The carbon selected was VULCAN XC-72, a high purity carbon with a N_2 BET surface area of 250 m^2g^{-1} and pore volume 3 ml g^{-1}. $H_2PtCl_6 \cdot 6H_2O$ (Fluka) was used as a platinum source. Hydrogen (IOL, India) was further purified by passing through a Pd Deoxo unit and a molecular sieve dehydrator. Carbon monoxide (Matheson, USA) was purified before use by passing through a molecular sieve trap. Benzene (Baker AR Grade, thiophene free) had a 99% purity and before using was distilled twice.

Method of Catalyst Preparation

Catalyst containing 5 wt.% platinum was prepared by incipient wetting of carbon with $H_2PtCl_6 \cdot 6H_2O$. An appropriate amount of $H_2PtCl_6 \cdot 6H_2O$ to yield the desired platinum loading was dissolved in a predetermined volume of double distilled water. The precursor solution under hot condition was added to carbon support under stirring. After drying at 120°C, the sample was reduced in a glass reactor at 250°C in flowing H_2 (40 ml min^{-1}) until it was free from chlorides, which was tested by absorbing off gases in water and adding $AgNO_3$ solution (20).

The physical mixtures of 5 wt.% Pt/C (PC-1) and carbon with various dilutions were prepared by grinding the mixtures mechanically for 30 min using an agate mortar and pestle. Care was taken to see that the grinding was done uniformly throughout for each mixture in order to obtain as homogeneous a mixture as possible. The obtained mixtures were heated in inert atmosphere at 400°C for 2 h and kept in a desiccator until use.

X-Ray Diffraction

The X-ray diffraction patterns were recorded on a Philips PW-1051 diffractometer by using Ni-filtered CuK_α radiation and standard conditions.

Chemisorption Measurements

A conventional pyrex glass high vacuum system having a stationary background vacuum of 10^{-6} Torr (1 Torr = 133.3 Pa), with a facility to reduce the sample *in situ* by flowing hydrogen, was used in all chemisorption experiments. The method of Benson and Boudart (21) and Wilson and Hall (22), in which the linear portion of the isotherm determined between 50 and 250 Torr is extrapolated to zero pressure, was used to determine hydrogen uptakes at ambient temperature. For determining CO uptakes the dual isotherm technique of Yates and Sinfelt (23) was used. In a typical experiment the catalyst sample (ca. 0.5 g) was placed in a U-shaped glass adsorption cell and was reduced by flowing hydrogen (30–40 ml/min) at 250°C for 6 h; then the sample was evacuated to 10^{-6} Torr at 400°C for 4 h in order to make sure that no residual H_2 was present. Then the sample was slowly cooled to ambient temperature where H_2 and CO uptakes were determined. Equilibration times of 1 h and 30 min were provided at each pressure for H_2 and CO chemisorptions, respectively.

Activity Studies

The benzene hydrogenation reaction was carried out in a continuous flow isothermal microreactor, interfaced by a six-way gas sampling valve with a gas chromatographic unit. After passing through a deoxo purifier and molecular sieve dehydrator the H_2 flow (40 ml/min) entered a benzene saturator kept in a thermostat at 30°C. The reactant mixture was then allowed to pass through a pyrex glass micro catalytic reactor (length = 20 cm; dia = 8 mm) having 0.2 g of catalyst kept between two quartz wool plugs. The reactor was heated by means of a vertical tube furnace and the reaction temperatures were maintained and measured by a Cr–Al thermocouple placed coaxially with the catalyst bed and a temperature controller. The reaction product obtained was only cyclohexane and was analysed by GC using a 10% carbowax 20 M on a chromosorb W column and flame ionisation detector.

RESULTS AND DISCUSSION

In the X-ray diffractogram of PC-1 and carbon-diluted PC-1 catalysts only a broad band was seen at approximately $2\theta = 24°$, which is due to the amorphous carbon itself. The absence of characteristic XRD lines due to platinum can be taken as an indication of high platinum dispersion on carbon; even if the crystallites are formed, they are too small to be detected by X-rays. The CO and H_2 chemisorption capacities and benzene hydrogenation activity data of PC-1 and carbon diluted PC-1 catalysts are presented in Table 1. On PC-1 sample a H_2 uptake of 81.7 μmol g^{-1}-cat (24) and a CO uptake of 54.8 μmol g^{-1}-cat (10) were found. Thus the PC-1 sample has a CO/H ratio of 0.35. This variation may be due to the fact that on metal sites CO chemisorbs in either linear or bridged form (25). High platinum loading results in large platinum crystals, and because of steric hinderance they adsorb much less CO increasing bridge bond participation (26). The increase in bridge-bonding participation in the case of highly dispersed catalysts seems to be contradictory to the results of Dorling and Moss (27) observed in the case of Pt/SiO_2, but our values are more similar to those described by Gruber (26) for Pt/Al_2O_3 and by Rodriguez-Reinoso *et al.* [28] for platinum supported on active carbon. It is possible to assume that the proportion of atoms

TABLE 1

Chemisorption Data and Activity Data Obtained at 25 and 100°C, Respectively, for PC-1 and PC-1 + C Physical Mixtures

Sample	Carbon	Pt[a]	N_{CO}[b]	N_H[c]	Total conversion	Percent conversion	QTOF	TOF
	PC-1	(mg)			(%)	(mg^{-1} Pt)	(mol h^{-1} g^{-1}-Pt)	(mol s^{-1} $site^{-1}$)
PC-1	0	10.000	3.30	9.84	85.8	8.6	0.5538	0.4694
PC-2	3 : 1	2.500	1.76	16.29	42.0	16.8	1.0844	0.1387
PC-3	9 : 1	1.000	0.72	20.34	26.1	26.1	1.6848	0.0690
PC-4	20 : 1	0.475	0.34	23.81	18.0	37.9	2.4458	0.0407
PC-5	50 : 1	0.195	0.14	21.49	11.0	56.4	3.6413	0.0275
PC-6	99 : 1	0.101	0.06	21.83	6.0	59.4	3.6409	0.0015

[a] Quantity of metal referred to the total weight of the catalyst bed.

[b] $N_{CO} = 10^{19}$ CO moleculed adsorbed per gram of sample.

[c] $N_H = 10^{19}$ H atoms adsorbed per gram of sample.

placed at edges and the imperfections in the crystallites will be greater for smaller particles, favouring bridged mode of CO chemisorption. However, a finite contribution due to hydrogen spillover in undiluted PC-1 itself cannot be ignored. A detailed characterisation using CO chemisorption, O_2–H_2 titration, and H_2 chemisorption was undertaken in our preliminary investigations on Pt/C catalysts with different Pt loadings (20, 29). It is worth mentioning here that the CO and H_2 uptakes were practically nil on carbon alone at room temperature.

It can be seen from Table 1 that N_{CO} values drop continuously with the addition of carbon to PC-1 catalyst. It is known that CO selectively chemisorbs on platinum. It can also be noted from Table 1 that with the degree of carbon addition the concentration of platinum in the total sample is decreasing and hence the decrease in CO chemisorption is taking place. Further, it can be noted that the amount of CO chemisorbed per mg of platinum is fairly constant in all the samples. If CO transfers by a spillover process, then more CO should spillover when additional carbon is placed in physical contact. However, unlike in the case of hydrogen, this is not observed, which may be because the heat of adsorption of CO, 31 Kcal mol^{-1}, is large when compared to the heat of adsorption of H_2, 19 Kcal mol^{-1}, on platinum surface (30–32). Hence CO molecules require a higher energy of activation to desorb from platinum surface and to further diffuse in order to spillover to another phase. Also, the kinetic results presented by Gland *et al.* (33) indicated that the displacement of CO from platinum requires a substantially large activation barrier when compared to hydrogen. As can be seen from Table 1 the N_H values continuously increased to a carbon dilution of 20 : 1 and beyond that decreased slightly and became constant. It is generally accepted that molecular hydrogen dissociates first on the metal sites into active mobile species which then migrates to the support sites (34), the support providing mainly the acceptor sites. Therefore, the increase in the N_H values with the dilution of PC-1 with carbon is mainly due to the increase in the number of support sites to accommodate the migrated hydrogen atoms which are initially formed on the metal sites. However, this migration process appears to be controlled by a distance factor also. The N_H value did not increase beyond PC-4 sample having the dilution ratio of 50 : 1. From this observation it appears that there may be a close and intimate contact between the metal site and the support site in order to facilitate the migration of hydrogen. The nature of the hydrogen acceptor sites probably varies from one acceptor material (generally the support) to another and has only been identified in a few cases. With respect to Al_2O_3 and SiO_2 it has been reported that surface hydroxyl groups of these supports are associated with acceptor sites for hydrogen (35, 36). In the case of carbon, it is known that the surface contains oxygen functional groups, carboxylic groups, and lactonic and phenolic groups with varied acid strengths consisting of both Lewis and Brønsted acid sites (37). Thus these surface functional groups may be associated with acceptor sites for hydrogen spillover on carbon. Knowledge of these functional groups and their nature of activity in Pt/C catalyst is reasonably precise (38). The surface contamination of platinum by small carbon particles formed from carbon functional groups during the reduction treatment of the catalyst (5, 6) and also during grinding (in case of physical mixtures) is possible. This contamination might act as a sort of "spillover bridge" to promote hydrogen migration to carbon from platinum site. The H_2 spillover on reducible oxides has recently been reported by Regalbuto and co-workers (39, 40), who have studied the effect of calcination on H_2 spillover in the Pt/MoO_3 system. On the basis of characterisation by electron microscopy and selective chemisorption and kinetics of H_2 spillover they concluded that overlayers of MoO_3 on Pt are produced which improve the degree of contact of MoO_3 with Pt crystallites, thus increasing H_2 spillover. Thus numerous studies suggest that H_2 spillover occurs via surface phase rather than through gas phase. Our H_2 chemisorption results clearly confirm the spilling of hydrogen at room temperature itself. Although it is evident that hydrogen migrates to support sites in atomic form, the exact nature of the spilled over species and the nature of active sites created is still under debate. Sheng and Gay (41) utilised solid state ^1H NMR to identify and study the adsorption and spillover of hydrogen on various platinum catalysts. From NMR investigations it appears that spilled over hydrogen may exist in a variety of states (charged, radical, or bound) depending on the catalyst systems and coadsorbing species. Several investigators (13, 42–49) identified the spilled over hydrogen species as protonic hydrogen, H^+. Other studies (49–52) conclude that the active species for hydrogen spillover is a hydrogen radical, $H^{\cdot}$. Bianchi *et al.* (53), in their study of hydrogen spillover from Pt/Al_2O_3 catalysts onto the methoxylated silica aerogel, even postulated an H_3^+ species on the basis of kinetic arguments.

Benzene conversion and conversion referring to unit weight (mg) of platinum, quasi-turnover frequency (QTOF), and turnover frequency (TOF) are given in Table 1. In our experiments the contact time expressed as W/F was chosen so as to have conversion levels which bring out better differences between the catalysts (PC-1 + carbon diluent) considered. Figure 1 shows the benzene conversion as a function of temperature at various levels of dilution of PC-1 catalyst. All curves show a maximum conversion around 100°C. The curve pattern reflects the positive influence of the reaction kinetics at lower temperatures, whereas at higher temperatures the thermodynamic effect prevails so the conversions decrease. Self-poisoning of benzene hydrogenation by irreversibly adsorbed benzene residues seems very probable even in the presence of H_2 and the extent of such self-poisoning would be expected to increase with increasing temperature. Numerous ultrahigh vacuum (UHV) (54–57) studies of benzene on platinum surface reveal that adsorption of benzene on Pt takes place via a π bond interaction in which the ring lies parallel to the metal surface. It was also reported that mode of benzene adsorption on Pt and support is similar although the bond strength may be somewhat higher on Pt (58, 59). Moreover benzene adsorbed on either of the surfaces can be removed by evacuation relatively at low temperatures (60, 61). From the results obtained in this study, however, the possibility of hydrogenation of benzene to cyclohexane being a reversible reaction and the equilibrium constant for the dehydrogenation increasing with temperature and rendering the hydrogenation of benzene less thermodynamically favoured at higher temperatures cannot be discounted. On the other hand, a reversible maximum in activity versus temperature for benzene hydrogenation has been reported frequently and has been explained successfully by assuming a decrease in the surface coverage of benzene at higher temperatures (62–64). The reversible maximum is also possible because of a decrease in chemisorption of H_2 (one of the reactants in reaction) at these moderately high temperatures (beyond 100°C) (64–66). It can be noted from Table 1 that the total conversion decreases with an increase of dilution level, whereas the conversion per unit weight of platinum (mg) in the catalyst is increasing. This shows a marked increase in the specific activity towards benzene hydrogenation to cyclohexane on Pt/C as a result of dilution with carbon. It should be noted that the activity of carbon on its own is negligible in the hydrogenation of benzene. This increase in the specific activity of the catalyst with dilution shows the involvement of carbon diluent in addition to platinum particles.

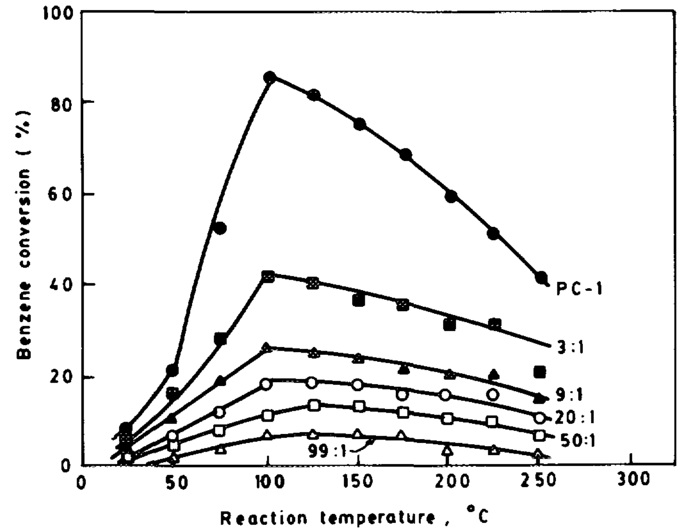

FIG. 1. Effect of temperature on benzene conversion over PC-1 (5 wt.% Pt/C) catalyst at various levels of dilution (1/3, 1/9, 1/20, 1/50, 1/99).

Although a detailed mechanism of the benzene hydrogenation in the presence of spilled over hydrogen is not known, evidence exists in the case of oxide supports. Acid sites, especially Brønsted sites, act as adsorption sites for benzene, and if activated hydrogen is available they can contribute towards catalyst activity (67–68). Ebitani *et al.* (69) reported that in the case of Pt supported on a SO_4^{2-} modified ZrO_2 system, hydrogen spillover from platinum can transfer electrons to Lewis acid sites and form protons, i.e., Brønsted acid sites on oxide surfaces. By analogy with the acid catalysed hydrogenation of benzene reported in homogeneous systems the formation of a carbonium ion from the interaction be-

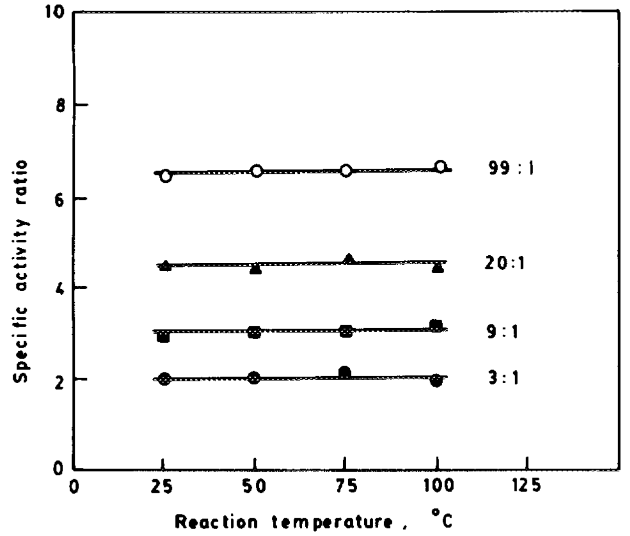

FIG. 2. Specific activity ratio (diluted/undiluted PC-1) as a function of temperature.

tween benzene and Brønsted acid sites seems reasonable and may represent the benzene hydrogenation mechanism on acidic surfaces (70, 71). More recently Lin and Vannice (72, 73) proposed that Brønsted acid sites or strong Lewis acid sites which can produce protons from spilled over hydrogen can activate benzene via the formation of a carbonium ion which can then be hydrogenated to cyclohexane by spilled over hydrogen. On the basis of evaluation of various reaction models they have postulated that the addition of the first H atom to the aromatic ring is the rate-determining step (RDS) as well as the concurrent formation of a predominant H-deficient surface species, and this is true in the case of spilled over hydrogen also. This model attributes the enhanced activity obtained with acidic supports to an additional metal support interfacial region in which the benzene adsorbs on acidic sites and reacts with the migrated hydrogen from metal surface. Several possibilities can be postulated concerning the reaction mechanism: (1) reaction of adsorbed benzene with adsorbed H_2 on Pt surface sites; (2) surface diffusion of spilled over H_2 to Pt surface sites followed by reaction on the Pt via a port hole effect; (3) reaction of the spilled over H_2 with adsorbed benzene on the carbon. Accordingly we suppose that a part of the reaction occurs by means of coadsorption of benzene and hydrogen on platinum, and that the other part occurs by means of their coadsorption on the carbon support sites as a result of the migration of some atomic hydrogen from metal to the support, thereby increasing the specific activity of the catalyst.

In Fig. 2 specific activity ratio is plotted as a function of temperature. The specific activity ratio varies from 2 to 6.5 for PC-2 to PC-6 samples in the dilution range of 3 : 1 to 99 : 1 and is independent in a temperature range of 25 to 100°C. Beyond 100°C the ratio (not shown in the figure) increases since with the increase of temperature the benzene conversion may decrease to different extents on PC-1 and PC-1 + C mixtures. It can also be noted from Table 1 that benzene conversion per (mg) platinum is increasing to PC-5 (50/1 dilution) and beyond that it remains constant. The same observation is made regarding the N_H values. Thus the hydrogen migration process appears to be controlled by a distance factor which plays an important role in determining specific activity of the catalyst. As the platinum is dispersed uniformly over entire surface of the carbon in case of PC-1, there is a high probability of collision between spilled over hydrogen atoms, and thus repeated formation of the molecular hydrogen, which is inactive in hydrogenating benzene molecule (18), may take place. Upon dilution, separation of single particles covered by platinum takes place and decreases the collision rate. This means that the stability of active centres increases and promotes the activity of the catalyst per unit weight of platinum. This appears to be valid up to a dilution of 50 : 1 and further dilution brings no benefit. From this it may be concluded that atomic hydrogen cannot migrate beyond certain distances depending on the texture of the physical mixture, i.e., catalyst + diluent. Sancier (17) found values ranging from 500 to 20,000 Å in the case of H_2 spillover on Pd/Al_2O_3. However, there must be a point where the additional surface area of the diluent brings no further benefit to the reaction.

Figure 3 presents the benzene conversion as a function of platinum concentration present in the total weight of catalyst bed at T = 100°C. The conversions increase with

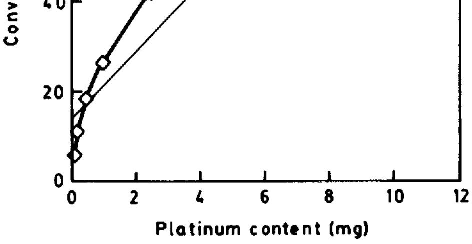

FIG. 3. Percent total conversion of benzene vs platinum content present in PC-1/PC-1 + carbon mixtures.

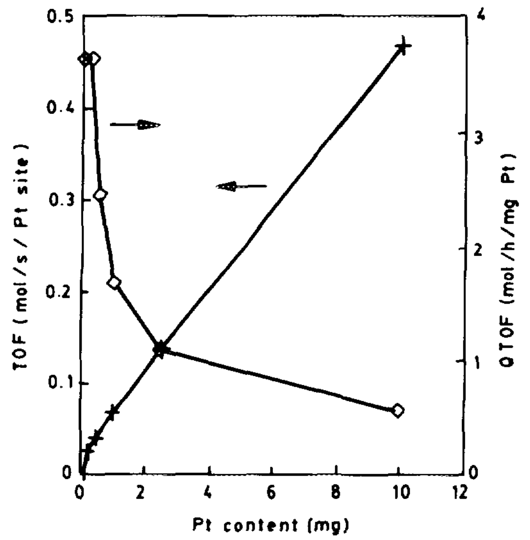

FIG. 4. Effect of Pt content on QTOF and TOF.

the platinum content for all degrees of dilution of the catalyst. Although conversions are not increasing linearly with platinum content, the related points for Pt/C + C catalysts fall fairly closely towards a straight line, indicating that the spillover level remains more or less constant and depends on the diluent surface. In fact the conversions are proportionally greater with the degree of dilution. This increase in the activity can be ascribed to the greater distance of the metal concentrations, i.e., 5 wt.% Pt/C in carbon diluent. 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 of PC-1 + C mixtures. It is on the distance of the individual granules of PC-1 that the spilled over H_2 concentration available for the reaction of the benzene over carbon support sites depends. In Fig. 4 TOF, i.e., the number of benzene molecules converted per site per second, and QTOF, defined as the number of moles benzene converted per hour per milligram platinum, are plotted as a function of platinum content present in the catalyst. In the case of PC-1 TOF is defined as per number of platinum surface sites, whereas in the case of PC-2 to PC-6, where hydrogen spillover situation exists, TOF is defined as per platinum sites plus sites in the support produced by spillover of chemisorbed hydrogen since N_H values of physical mixtures (PC-2 to PC-6) represent platinum surface sites as well as support sites produced because of hydrogen spillover. Here it may be assumed that the extent of H_2 spillover at 25°C is equivalent to that at the reaction temperature of 100°C since the number of Pt sites which are H atom generators are reported to be the same at 25 and 100°C. Although an increase in H_2 adsorption is observed with a rise in temperatures (beyond 25°C) the increment is attributed mainly to multiple bond adsorption or reversible H_2 adsorption on metal sites since it is well established that strong and irreversible H_2 uptake which corresponds to 1 : 1 stochiometry of H/metal does not change with temperature (64–66). Generally the capacity of metal atoms to form multiple bonds with hydrogen atoms on the catalyst surface is enhanced by a rise in the temperature. In Fig. 4 it can be seen that TOF is decreasing linearly with decrease in platinum content which is a measure of the ratio of benzene molecules converted and number of active sites present. It is more appropriate here to express the activity of the catalyst as QTOF, which is an apparent value

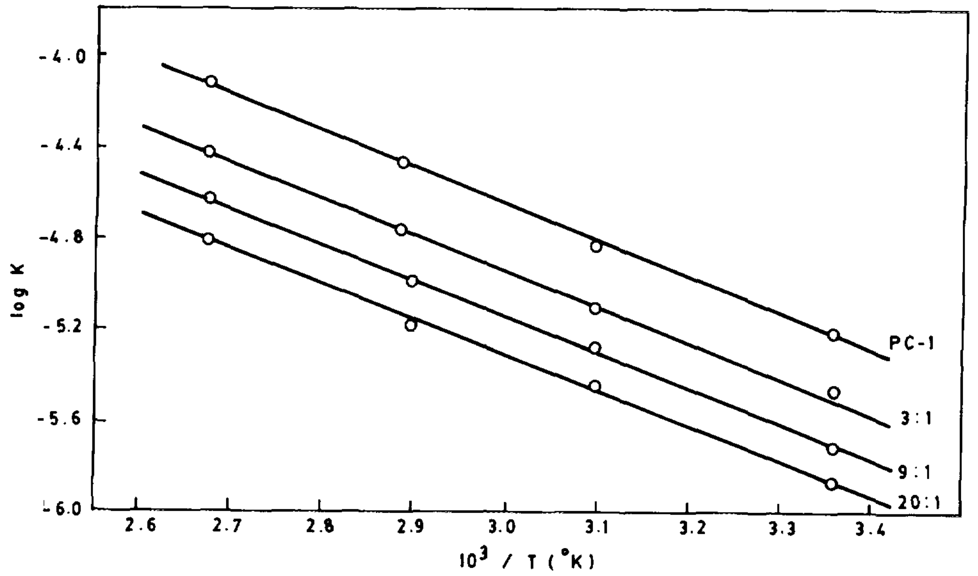

FIG. 5. Arrhenius plots for PC-1 and PC-1 + carbon mixtures (1/3, 1/9, 1/20).

since both platinum surface sites as well as support sites are participating in the existing situation of H_2 spillover. It can be seen from Fig. 4 that QTOF is increasing with a decrease in platinum content in the catalyst. The trend observed in QTOF values clearly reflects the part played in benzene hydrogenation by support sites as a result of spillover. In other words QTOF shows that the specific activity of the catalyst is increasing upon dilution of PC-1 with carbon because of hydrogen spillover.

The Arrhenius plots of PC-1 and diluted PC-1 samples are illustrated in Fig. 5. The results show an apparent activation energy value of 8.27 Kcal/mol. The calculated surface diffusion energy of active hydrogen on carbon is 39.2 Kcal/mol (5), which greatly exceeds the experimental value, and thus the reaction is not controlled by surface diffusion of atomic hydrogen. As a result the reaction follows the same path on both the platinum sites and carbon sites. Then the rate-determining step on diluent surface is the reaction between adsorbed benzene and spilled over hydrogen (18). From our activity results we can say that the mechanism followed by benzene hydrogenation with spilled over hydrogen is same irrespective of the support used.

CONCLUSIONS

H_2 spillover was observed at ambient temperature on carbon-supported platinum. CO and H_2 chemisorptions exhibit contrasting trends on Pt/C diluted, with carbon showing that while H_2 migrates over to the carbon support, CO does not. Benzene hydrogenation activity data suggest that upon dilution with carbon the specific activity of Pt/C catalyst increases to a dilution of 50 : 1, beyond which it becomes constant. The fact that H_2 spillover is taking place on Pt/C diluted by carbon at 25°C is confirmed by hydrogen chemisorption and benzene hydrogenation data.

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