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Benzene Hydrogenation over Supported and Unsupported Palladium

I. Kinetic Behavior

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The kinetics of benzene hydrogenation over supported Pd catalysts and unsupported Pd powder were examined under a wide range of reaction conditions. At temperatures below 433 K, apparent activation energies were routinely near 12.0 kcal $mole^{-1}$. The reaction order in hydrogen for supported catalysts increased from 0.5 to nearly 4 as the temperature increased from 353 to 573 K, and this same parameter for Pd powder showed a similar trend but was more temperature sensitive. The reaction order in benzene increased from zero to 0.8 over the same temperature range but a smaller difference was observed between the results obtained for supported and unsupported Pd. The activity of all the samples showed a temperature-dependent maximum near 495 K, but the unsupported Pd had a greater tendency to exhibit deactivation, which was attributed to carbonaceous surface species formed from reversible dehydrogenation of adsorbed benzene. The lowest turnover frequencies occurred on the Pd powder whereas values 10–50 times higher were obtained over low-temperature reduced Pd catalysts prepared using Cl-containing precursors and acidic supports such as SiO_2–Al_2O_3 and TiO_2. The enhanced activity over these last two catalysts is attributed to additional benzene adsorption sites present on the support surface in the metal–support interfacial region.

INTRODUCTION

Benzene hydrogenation is a reaction readily catalyzed by most Group VIII metals; however, it has been found that the specific activity of Pd catalysts for benzene hydrogenation can be enhanced if acidic supports such as SiO_2–Al_2O_3 or zeolites are used (*1*). These supports by themselves do not catalyze the reaction; consequently, one explanation for this reported support effect has been that a metal–support interaction exists which changes the chemical properties of the dispersed metal (*1*). However, another possibility is that this activity enhancement could be due to the creation of additional active sites at the metal–support interface (*2*, *3*). In an attempt to elucidate the nature of this support effect, kinetic data for benzene hydrogenation have been collected over a wide range of reaction conditions using a family of Pd catalysts with significantly different specific activities.

Although benzene hydrogenation over Pd catalysts produces only cyclohexane and appears to be rather straightforward, this reaction does present the following interesting feature: At temperatures below 433 K the reaction follows a simple Arrhenius law, but it shows a temperature-dependent maximum near 495 K (*3*). In addition, both Pd/SiO_2–Al_2O_3 and Pd/TiO_2 catalysts exhibited unusually high specific activities, but only when reduced at low temperature (*3*). To better understand this behavior, a series of supported Pd catalysts and an unsupported Pd powder were examined and compared. Results showed that many aspects of the benzene hydrogenation kinetics were very similar over all the supported Pd catalysts, regardless of their activity. However, unsupported Pd powder showed distinctively different kinetic behavior in some regards, compared to the

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supported catalysts, and this difference suggested a possible explanation as to why acidic supports can enhance the activity for benzene hydrogenation when normalized to surface Pd atoms. The kinetic data are presented in this paper, and the support effect on specific activity is discussed. A detailed Langmuir–Hinshelwood-type model which describes the kinetic behavior of this reaction over Pd catalysts is proposed in a following paper (*4*).

EXPERIMENTAL

Catalyst Preparation

Support materials used in this study were SiO_2 (Davison Grade 57, 220 $m^2\ g^{-1}$), SiO_2–Al_2O_3 (Davison Grade 979, 13% Al_2O_3, 400 $m^2\ g^{-1}$), η-Al_2O_3 (Exxon Research & Engineering Co., 245 $m^2\ g^{-1}$), and TiO_2 (Degussa P25, 80% anatase and 20% rutile, 50 $m^2\ g^{-1}$). Supported catalysts were prepared by impregnating the supports with an aqueous solution of H_2PdCl_4 prepared from $PdCl_2$ (Ventron Corp.) and dilute hydrochloric acid. These catalysts were then dried in air at 393 K overnight. Unsupported Pd samples were prepared by reducing PdO (Strem Chemicals) in 70 $cm^3\ min^{-1}$ of a 10% H_2, 90% He mixture for 1 h at 373 K followed by a 2-h reduction at 473 or 573 K. The pretreatment of the catalysts, carried out *in situ* before each kinetic experiment, consisted of a 30-min treatment in 50 $cm^3\ min^{-1}$ of He at a temperature ranging from 448 to 533 K and a 1-h reduction in 50 $cm^3\ min^{-1}$ of H_2 at 0.1 MPa at a temperature ranging from 448 to 673 K. Further details of the preparation method and pretreatments have been described elsewhere (*3*). The Pd weight loadings were determined by plasma emission spectroscopy and neutron activation analysis. Following the kinetic studies, H_2 and CO chemisorption at 300 K on these used samples was measured in a glass volumetric adsorption system using a method involving two isotherms (*5*). Oxygen uptakes were determined by extrapolating adsorption isotherms measured at 300 K to zero pressure to correct for any physisorbed oxygen on the supports.

Benzene Hydrogenation

All the kinetic data were obtained in a microreactor system described elsewhere (*6*). Ultrahigh purity H_2 and He (both 99.999% from Linde Specialty Gases) were further purified by passing these gases through Oxytraps (Alltech Associates), and gas flow rates were measured by mass flow meters (Hasting–Raydist). Benzene (Baker analyzed, residue after evaporation—4 ppm, thiophene < 1 ppm) was degassed in He at 343 K for 20 min before each experiment and kept in a glove bag constantly flushed with He. Benzene was introduced into the reaction system by a calibrated Rainin peristaltic pump and vaporized in the reactor inlet line, which was wrapped with heating tapes. The benzene flow rate was simultaneously monitored using a pipet, calibrated in 0.01-ml subdivisions, which served as a temporary reservoir for the pump during the measurements. Benzene and cyclohexane were analyzed by a Hewlett–Packard Model 700-00 gas chromatograph using 1,2,3-tris(2-cyanoethoxy) propane (Supelco, Inc.) as the column packing, and conversions of benzene were kept below 10% to avoid heat and mass transfer effects by using different catalyst sample sizes for different reaction temperature ranges. For each data point, a bracketing technique was followed which consisted of a 25-min period for the system to reach steady state, a 15-min period for sample analysis, and a 25-min period under pure H_2 for regeneration of the catalyst and adjustment of reaction conditions for the next data point. After collecting data under a range of reaction conditions, the experiments were repeated by changing conditions in the reverse order to check for possible deactivation of the catalyst.

RESULTS

At temperatures below 433 K, the reaction rates measured for each sample produced a linear Arrhenius plot, as shown in Fig. 1. The activation energies, activities, and hydrogen chemisorption uptakes on used samples are listed in Table 1, where the turnover frequency, TOF, is defined as benzene molecules converted per surface Pd atom per second. Some results reported in the literature are also listed in the table for comparison after adjusting TOF values to the same reaction conditions (*1, 7–10*). As the temperature increases, the activities of all the samples reach a maximum near 495 K and then decrease at higher temperatures (Fig. 2), although conversions were always kept far below the equilibrium benzene conversion (0.99 at 495 K under these conditions). For the supported catalysts the temperature-dependent maximum was quite reversible, and it could be traversed from either the high- or the low-temperature side; however, although the Pd powder exhibited the same activity maximum, noticeable deactivation of the unsupported Pd sample occurred if the reaction temperature were increased beyond 493 K even though the H_2 bracketing technique was used. If the experiment with the Pd powder was repeated immediately after completion of a run, the activity followed the lower curve of run d in Fig. 2a, and no further deactivation was observed. In a separate experiment, the original activity of the Pd powder (run h in Fig. 2b) was completely recovered by an overnight regeneration in 50 cm^3 min^{-1} pure hydrogen at 383 K.

Reaction orders in H_2 and benzene were determined in 50-Torr benzene and 600-Torr H_2, respectively, and typical sets of data are shown in Fig. 3. These plots of ln(activity) versus ln(*P*) were usually linear when reaction temperatures were below 593 K. In order to obtain measurable con-

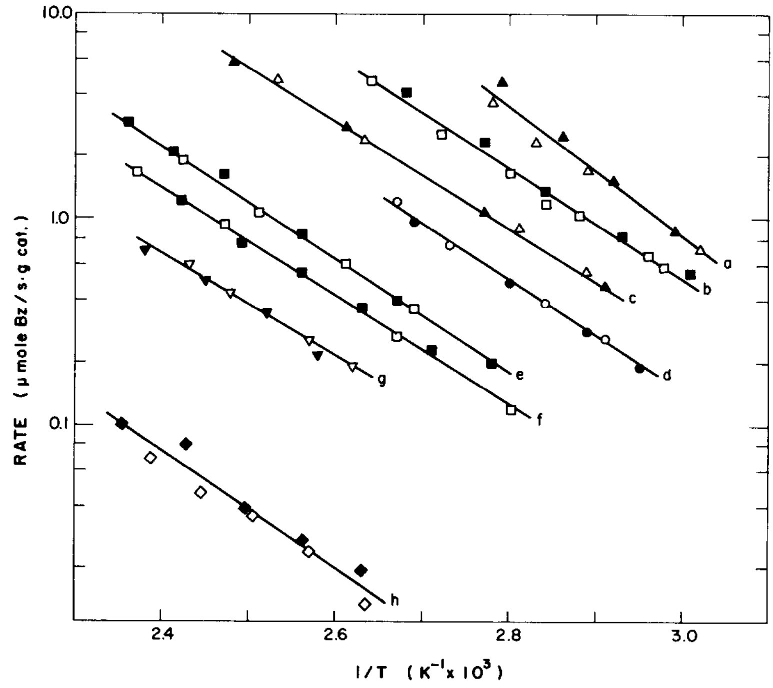

FIG. 1. Benzene hydrogenation activity over Pd catalysts at 50 Torr benzene, 680 Torr hydrogen, and temperatures below 433 K: 2.03% Pd/TiO_2 (I)—b, (III)—e, (IV)—f; 1.95% Pd/SiO_2–Al_2O_3 (I)—a, (II)—c; 1.80% Pd/Al_2O_3 (II)—d; 1.71% Pd/SiO_2 (II)—g; Pd powder—h. (Roman numerals indicate sample numbers. Open symbols, data collected in sequence of increasing temperature; closed symbols, decreasing temperature.)

TABLE 1

Adsorption Behavior and Kinetic Parameters for Benzene Hydrogenation on Palladium Catalysts

Catalyst (sample)	T_r (K)	Chemisorption[a] (μmole/g cat.)			d[b] (nm)	E_a[c] (kcal/mole)	Activity[d] (μmole Bz/s · g cat.)	TOF[d] (s^{-1})			Ref.
		H_2	O_2	CO				(1)	(2)	(3)	
2.03% Pd/TiO_2											
(I)	448	20	14	29	5.4	12.3	18.5	0.463	0.661	0.638	
(I-C)[e]	448	17	23	62	6.3	14.2	25.3	0.743	0.549	0.407	
(II)	523	13	13	25	(8.3)	12.3	2.8	0.113	0.113	0.113	
(III)	593	7	14	24	(15.4)	12.4	2.0	0.140	0.070	0.082	
(IV)	673	6	16	16	(18.0)	11.9	1.2	0.104	0.039	0.077	
(V)	773	3.5	16.5	7	(30.8)	11.3	0.5	0.071	0.015	0.071	
0.39% Pd/TiO_2	448	4	5.5	12	5.2	11.9	6.2	0.777	0.545	0.515	
1.95% $Pd/SiO_2–Al_2O_3$											
(I)	448	24	20	52	4.3	14.2	53.4	1.112	1.059	1.027	
(I-C)[e]	448	33	23	69	3.1	14.2	34.6	0.523	0.447	0.501	
(II)	673	23	31	54	4.5	11.7	7.6	0.166	0.123	0.141	
1.80% Pd/Al_2O_3											
(I)	448	28	23	68	3.4	12.6	7.9	0.149	0.181	0.122	
(II)	673	31	24	54	3.1	12.4	5.6	0.091	0.116	0.104	
1.71% Pd/SiO_2											
(I)	448	6	2	13	15.1	12.2	1.8	0.154	0.420	0.147	
(II)	673	5	5	14	18.2	11.3	0.6	0.060	0.063	0.043	
1.36% Pd/C	673	1.3	8.5	17	55.5	8.5	0.06	0.022	0.005	0.003	
Pd powder	473	1.6	2.2	9.6	1000	12.9	0.064	0.020	0.015	0.006	
Pd/SiO_2	673					14.0		0.035			7
Pd/Al_2O_3	673				10.5			0.012–0.018[f]			8
Pd/zeolite	573					8.5–11.0[f]		0.070–0.280[f]			1
$Pd/SiO_2–Al_2O_3$	673							0.125–0.250			1
Pd/SiO_2	673							0.060			1
Pd/Al_2O_3	673							0.075			1
Pd/SiO_2	573–773							0.026–0.028[f]			9
Pd/Al_2O_3	573–773							0.061–0.075[f]			9
Pd/SiO_2	573–773							0.015–0.082[f]			10

[a] Uptakes on used samples.

[b] Pd crystallite size based on hydrogen chemisorption. Values calculated for Pd/TiO_2 samples reduced above 448 K are overestimated to some extent due to site blockage (see text).

[c] Activation energies measured between 323 and 423 K.

[d] Activity at 413 K, 680 Torr H_2, and 50 Torr benzene. TOF based on chemisorption of (1) H_2, (2) O_2, (3) CO.

[e] Samples calcined at 773 K in flowing air before reduction.

[f] Values reported for several different samples.

versions, yet keep them below 10%, three different sample sizes of each catalyst were used to cover the temperature range from 373 to 593 K. The activity per unit mass of each catalyst sometimes differed slightly from one load to another, probably due to small differences in Pd dispersion, but the difference did not affect the reaction orders determined from these data. As shown in Fig. 4, the reaction order in H_2 increased with reaction temperature from near 0.5 to nearly 4 while the reaction order in benzene changed from near zero to above 0.5. The reaction orders measured for 2.03% Pd/TiO_2 (Sample I, T_r = 448 K) were obtained at temperatures below 448 K because the activity of this catalyst was found to be very sensitive to the reduction temperature (*3*), and therefore measurements at temperatures above the reduction temperature would complicate interpretation of the data. Reaction orders measured for unsupported Pd samples were somewhat different from those measured for supported Pd samples in two respects: the reaction order in hydrogen was more sensitive to temperature and the reaction order in benzene appeared to reach a maximum near 473 K.

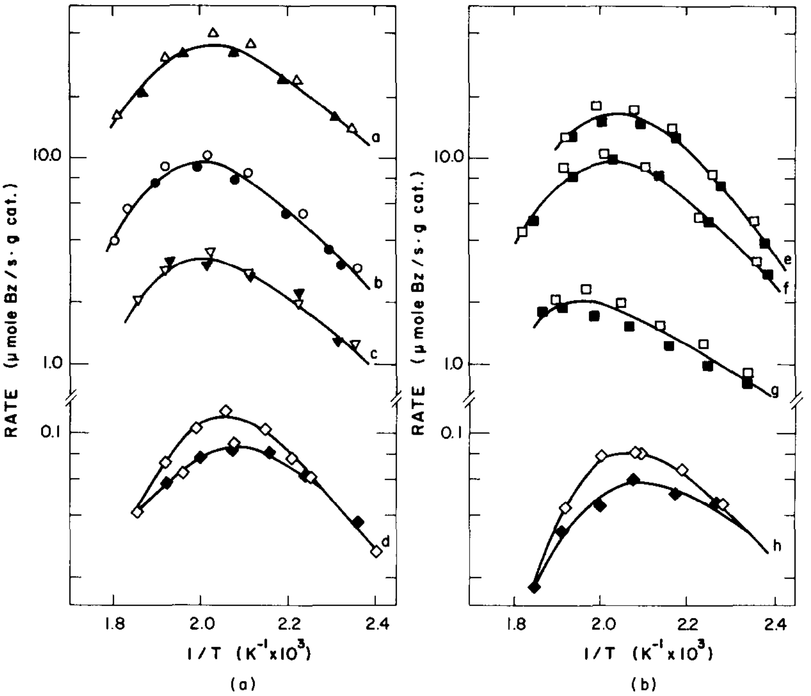

FIG. 2. Activities of Pd catalysts for benzene hydrogenation above 433 K: 2.03% Pd/TiO_2 (II)—e, (III)—f, (VI)—g; 1.95% $Pd/SiO_2–Al_2O_3$ (II)—a; 1.80% Pd/Al_2O_3 (II)—b; 1.71% Pd/SiO_2 (II)—c; Pd powder—d, h. (Upper curve of h also contains results after regeneration in H_2 overnight.) Open symbols—increasing temperature, closed symbols—decreasing temperature.

DISCUSSION

The data in Table 1 from this study show that $Pd/SiO_2–Al_2O_3$ and Pd/TiO_2 catalysts can be much more active than Pd/SiO_2 and Pd/Al_2O_3 catalysts. These results are consistent with earlier investigations which indicated that activities of supported Pd catalysts for benzene hydrogenation increase with the acidity of the support (*1*). However, as shown in Fig. 5, two of the catalysts studied (2.03% Pd/TiO_2, Sample I, and 1.95% $Pd/SiO_2–Al_2O_3$, Sample I) were two to three times more active than the most active Pd catalysts reported in the literature. Activities of these two samples decreased somewhat after a calcination at 773 K in flowing air for 2 h and a reduction at 448 K, but still remained higher than the other samples. Figueras *et al.* (*1*) have suggested that this support effect is a consequence of charge transfer from Pd to electron-acceptor sites on the support. However, their evidence was based on changes in the IR spectra of chemisorbed CO, and recent studies have indicated that shifts in the IR spectra of adsorbed CO reflect mainly the coordination number of surface Pd atoms rather than changes in electron density (*11*, *12*). Furthermore, an explanation based only on charge transfer does not readily explain other support effects observed for different reactions on different metals. For example, Pd/SiO_2 and Pd/Al_2O_3 catalysts show comparable activities for benzene hydrogenation (*1*, *3*); however, Pd/Al_2O_3 is much more active than Pd/SiO_2 for CO methanation (*13*). Also, when these two oxides are used to disperse Ni, support effects in the CO methanation reaction again become insignificant (*14*).

A more consistent explanation can be based on the proposal that the observed support effect is a consequence of the di-

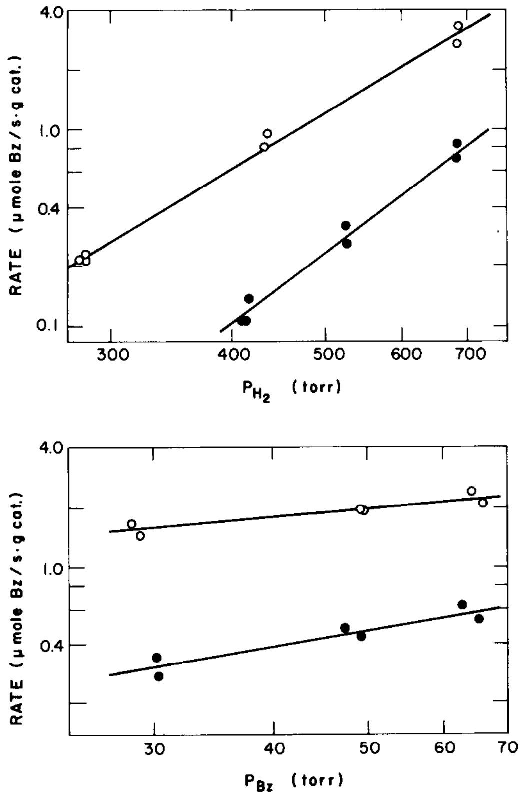

FIG. 3. Pressure dependencies on H_2 and benzene of benzene hydrogenation over 1.80% Pd/Al_2O_3. Reaction conditions, Upper figure—50 Torr benzene; Lower figure—600 Torr H_2. (Open symbols, 553 K; closed symbols, 573 K).

rect involvement of the support in the reaction process. In the case of CO methanation, Lewis acid sites on the support may assist the dissociation of CO (*15–17*), and therefore Al_2O_3 can enhance the activity of metals on which the rate is controlled by this step. In the case of benzene hydrogenation, since support effects are more pronounced with SiO_2–Al_2O_3 and zeolites, Brønsted acid sites appear to be more important. Peri has shown that benzene adsorbs on acid sites existing on oxide surfaces (*18*); consequently, it is expected that benzene can adsorb on acid sites which exist in the metal–support interface region and will readily react with hydrogen activated by the metal (*3*). In fact, a correlation between the amount of benzene adsorbed on the support and the activity of this reaction over Ni/TiO_2–ZrO_2 catalysts has recently been reported (*19*). From a UV and IR spectroscopic study, Primet *et al.* (*2*) have proposed that benzene adsorbed on a zeolite migrates toward the metallic phase, Pt in their case, to be hydrogenated. Their results also indicated that hydrogenation of the benzene adsorbed on the support was completed before the concentration of benzene on the metal surface began to decrease; therefore, their results also imply a feasible reaction path involving sites on the support. These sites, most likely Brønsted acid sites, are commonly found on SiO_2–Al_2O_3 and zeolites and can also exist on titanias which contain impurities (*20*).

In relation to the acidity of the support, other factors such as the presence of chloride on the surface and the reduction temperature can have a significant effect on the activity (*3*). Both Pd/TiO_2 and Pd/SiO_2–Al_2O_3 catalysts prepared from $PdCl_2$ showed a much higher activity when these catalysts were reduced only at low temperatures (448 K). Since an activity increase was observed with both supports, the effect of reduction temperature is *not* related to the "strong metal–support interaction" often proposed to explain the suppression of chemisorption on TiO_2-supported catalysts after a high-temperature reduction (HTR) (*21*). This was further confirmed by the fact that a Pd/TiO_2 catalyst prepared from a Pd precursor containing no chlorine and reduced at 448 K had a specific activity (TOF) comparable to the Pd/TiO_2 catalysts after HTR; but addition of chloride by impregnation with HCl again caused a significant activity enhancement (*3*). Apparently, additional sites can be generated from either Cl contained in the Pd precursor or Cl added directly.

Recently, the effects of chloride on the benzene hydrogenation activities of Rh/Al_2O_3, Rh/SiO_2, Ir/SiO_2, and Ir/TiO_2 were investigated by Marques da Cruz *et al.* (*22*) and Tiep *et al.* (*23*). Although these authors

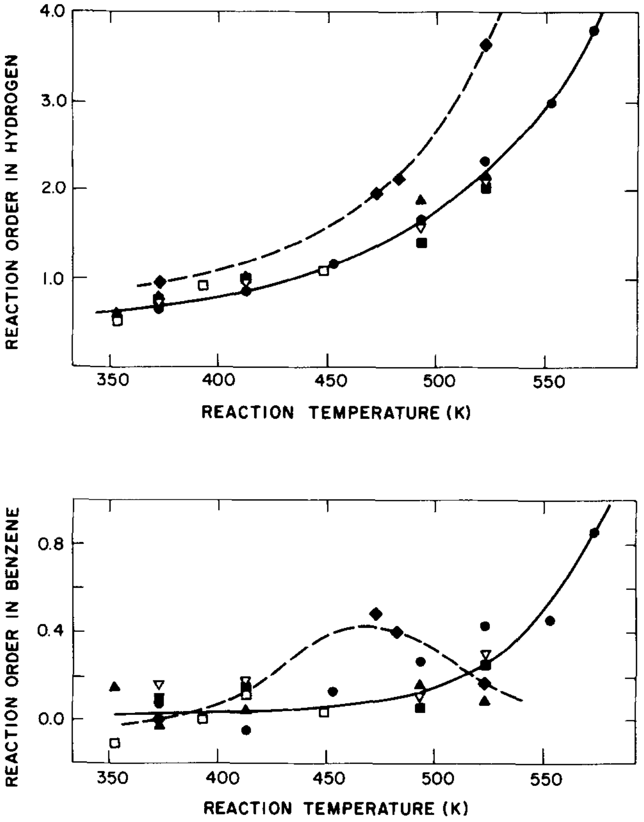

FIG. 4. Reaction orders of benzene hydrogenation on Pd catalysts: 2.03% Pd/TiO_2 (I)—□, (IV)—■; 1.95% Pd/SiO_2–Al_2O_3 (II)—▲; 1.80% Pd/Al_2O_3 (II)—●; 1.71% Pd/SiO_2 (II)—▽; Pd powder (T_r = 573 K)—◆.

suggested that no effect of chloride was observed, their results are actually in good agreement with our previous findings because (1) the effects of chloride were observed only when the catalysts were reduced at low temperature (448 K); (2) the effects were observed when SiO_2–Al_2O_3 or TiO_2 was used as the support, but they were much less significant with SiO_2 or Al_2O_3; and (3) the HTR step at 773 K caused a sharp decrease in hydrogen and CO chemisorption on the TiO_2-supported catalysts but not in the TOF, when compared with the more typical catalysts. In regard to the last observation, the TOF on the Ir/TiO_2 (HTR) catalyst in Ref. (*23*) was undoubtedly underestimated because oxygen chemisorption was used to count the number of surface Ir atoms. Much recent evidence has shown that during an HTR step TiO_x species can migrate onto metal surfaces and block chemisorption sites (*24*, *25*). However, this coverage does not appear to effect the oxygen uptake to the same extent, as shown by Meriaudeau *et al.* (*26*) and the results in Table 1. This is because large irreversible uptakes of O_2 occur on titania surfaces after an HTR pretreatment (*27*). Consequently, the number of exposed Ir atoms in the Ir/TiO_2 (HTR) samples would be much smaller than that determined from uncorrected oxygen uptakes or H_2–O_2 titrations. The anticipated correction to decrease the number of Ir surface atoms would make their results quite consistent with ours.

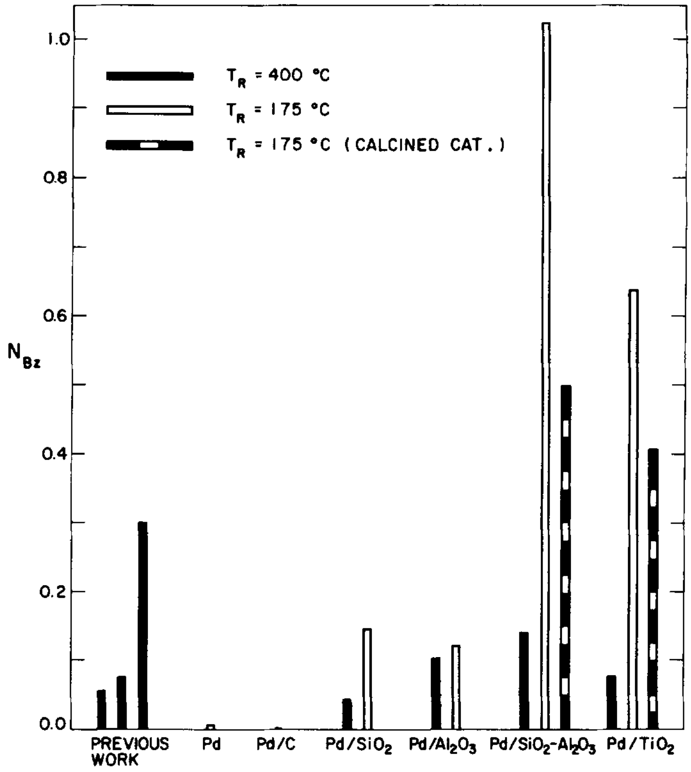

FIG. 5. Turnover frequency, N_{Bz} = molecules Bz · s^{-1} · Pd_s^{-1}, for benzene hydrogenation over Pd catalysts at 50 Torr benzene, 680 Torr hydrogen, and 413 K. (N_{Bz} based on CO chemisorption assuming CO_{ad}/Pd_s = 1.)

It is known that halogens can polarize surface hydroxyl groups on oxides and increase their acidity (*28*), and hydrogen chloride generated during the reduction in catalysts prepared from $PdCl_2$ can adsorb on certain supports like TiO_2 and produce strong acidic sites (*29*). Also, HCl adsorbed on oxides can be removed at high temperatures and the adsorption of HCl is greater on TiO_2 than on Al_2O_3 or SiO_2 (*29–31*). The observed activity enhancement is attributed to the chloride which can generate strong Brønsted acid sites but can be removed at relatively low temperatures. It has been shown that chlorination of Al_2O_3 at lower temperatures produces Brønsted acid sites while Lewis acid sites develop at higher temperatures (*32*). Using temperature-programmed reduction, Tiep *et al.* (*23*) showed that during the reduction in Ir/TiO_2 catalysts prepared from K_3IrCl_6, H_2O formation began at a fairly low temperature, as indicated by the hydrogen consumption, but HCl was not detected in the gas phase until the temperature approached 473 K, which is precisely the range of reduction temperature (448–523 K) in which the effects of chloride began to disappear (*3*). These results can explain why chloride effects have not been found to be significant either after HTR or when Al_2O_3 or SiO_2 was used as a support (*3, 9, 10, 33*). Although the nature of the active sites created by Cl is not fully understood at this point, the effect of chloride seems to be clearly established.

Kinetic data obtained at higher temperatures provided additional evidence that new active sites for benzene hydrogenation exist on the support. The activities of all the supported catalysts exhibited a reversible maximum near 495 K. Because benzene conversions were kept below 10% in these runs and the equilibrium conversion at 495 K remained near 99% under these reaction conditions, the decrease in activity with increasing temperature in Fig. 2 is not due to thermodynamic limitations. For a Langmuir–Hinshelwood-type surface reaction, such a maximum in reaction rate can occur because the positive temperature effect on the rate constant will eventually be offset by decreases in the surface concentrations of reactants at higher temperatures. Other causes for the activity maximum, such as sintering or poisoning at higher temperatures, are possible; however, the reversibility of the phenomenon observed with the supported catalysts eliminated sintering as a cause and, if it is due to a poison, the poison must be reversibly held and is therefore more appropriately considered as an inhibitor. Evidence of inhibition at higher temperatures is quite obvious for the unsupported Pd samples, as shown in Fig. 2, and although these samples can be completely regenerated in pure hydrogen, the process is relatively slow. The significance of these results is twofold: first, some deactivation of these catalysts can occur at higher temperatures, at least on the Pd surface, and second, there appears to be two types of sites for the reaction, with those sites on the metal being more susceptible to inhibition than those proposed to exist on the oxide surface in the metal–support interfacial region.

A sample of TiO_2 impregnated with a dilute HCl solution showed no detectable activity for benzene hydrogenation up to 433 K; therefore, the major role of the support in the enhancement of benzene hydrogenation activity is presumed to be to provide additional sites for benzene adsorption and to destabilize the aromatic ring. Because of the similarity of reaction parameters, benzene adsorbed on the support in the vicinity of sources of activated hydrogen, i.e., the Pd particles, is apparently hydrogenated in a reaction sequence similar to that for benzene adsorbed on Pd. Although activated hydrogen may have to migrate off the Pd surface to react with benzene, the very similar TOFs measured after reduction at 448 K for two catalysts with equal dispersions but different loadings (2.03% Pd/TiO_2 and 0.39% Pd/TiO_2) suggest that hydrogen migration distances are very short and the reaction is limited to the metal–support interfacial region.

The inhibition is most likely due to species generated by the dehydrogenation of adsorbed benzene, and evidence for the dehydrogenation of unsaturated hydrocarbons on metal surfaces is abundant. Hydrogen–deuterium exchange between C_6H_6 and C_6D_6 on metal surfaces indicates that the breaking of C–H bonds occurs on metal surfaces (*34*). The adsorption of unsaturated hydrocarbons on metal surfaces often leads to H_2 desorption and residual hydrocarbon species which cannot be removed unless treated with hydrogen (*35–39*). Self-hydrogenation of unsaturated hydrocarbons on metal surfaces has also been reported (*40*). By measuring changes in the magnetization of certain metals, one can estimate the number of chemisorption bonds formed between an adsorbed molecule and the metal surface. Silvent and Selwood (*41*) and Martin and Imelik (*42*) have reported that the bond number for a benzene molecule on Ni increased from 6 at temperatures below 375 K to 18 at 473 K. Because the carbon ring remained intact after the experiment, their results suggested essentially complete dehydrogenation of benzene on Ni at temperatures close to that where the activity maximum occurs on Pd, and a similar maximum has been observed on other Group VIII metals including Ni (*6, 43–46*). Dehydrogenation of some unsaturated hydrocarbons on metal surfaces was so severe that Beeck (*40*) reached the conclusion that adsorbed ethylene was inactive and resulted in self-poisoning of the hydrogenation reaction.

Beeck also associated the extent of poisoning with the heats of adsorption of hydrogen and the hydrocarbon on metals, which can be considered as the driving force for the dehydrogenation of the initial adsorbate.

Similar evidence for the dehydrogenation of unsaturated hydrocarbons on oxides also exists. For example, H_2–D_2 exchange between unsaturated hydrocarbons on oxides has been reported (*47*), and coke formation on cracking catalysts suggests that dehydrogenation can also be severe on oxides at high temperatures. However, because of the absence of unfilled *d* orbitals, pure oxides are expected to be much less active catalysts for hydrocarbon dehydrogenation than Group VIII metals, and this may explain why interfacial sites in supported Pd samples are less susceptible to inhibition at higher temperatures. Pd plays a major role in activating hydrogen in addition to providing sites for benzene adsorption. Since benzene does not cover the entire metal surface (*36*) and adsorption sites for hydrogen can exist between carbon rings, species formed from the dehydrogenation of benzene might be expected to have little effect on H_2 dissociation and activation on the metal surface unless the carbon ring disintegrated. The occurrence of H_2–D_2 exchange over oxides activated at high temperatures suggests that oxides are also capable of activating hydrogen; however, oxides generally have much lower site densities than metals, and hydrocarbons can easily block these sites and significantly inhibit such exchange reactions (*48*).

The proposal that self-inhibition of benzene occurs on these catalysts is further supported by the reaction orders determined from the kinetic data. The rate dependence on hydrogen increases from 0.5 at low temperatures to nearly 4 at high temperatures. The proposal that the rate-determining step (RDS) shifts from the addition of the first hydrogen atom to that of the last hydrogen atom to the ring as reaction temperature increases results in the prediction of a maximum reaction order in hydrogen of 3.0, but no higher. However, if dehydrogenation of adsorbed benzene to form additional surface species is included in the model, an additional effect must be considered because some of the active sites on the Pd can be covered by these inactive carbonaceous species. The consequences of this more refined kinetic model are discussed in detail in the following paper (*4*).

Bifunctional catalysis is an accepted concept in many reactions involving carbonium ion chemistry, but the possible role of the support in facile reactions such as benzene hydrogenation has not been frequently considered. However, a hydrogenation reaction mechanism involving carbonium ions has been suggested for catalysts such as these (*49*), and the concept of metal–support interfacial sites, i.e., adlineation (*50*), has been proposed for hydrogenation reactions decades ago (*51*).

SUMMARY

The activities for benzene hydrogenation over Pd catalysts prepared from $PdCl_2$ dispersed on certain oxides can be significantly increased if the catalysts are reduced only at low temperatures (448 K). The most straightforward explanation for this enhancement is that additional active sites for benzene are created in the metal–support interface region which increases the surface concentration of adsorbed benzene. These adsorption sites are proposed to be acid sites, most likely Brønsted acid sites, whose concentration on certain oxides can be increased by the presence of chloride. Although Pd catalyzes the reaction, kinetic data indicate that benzene adsorbed on Pd tends to undergo increased dehydrogenation at higher temperatures and to form carbonaceous species which reduce the number of available active sites on the Pd surface. We propose that the benzene adsorbed on acidic sites on the oxide surface near Pd particles in the adlineation region also reacts with hydrogen activated by Pd in a manner similar to benzene adsorbed on

Pd surface itself, but these sites are less susceptible to deactivation. Consequently, steady-state specific activities are greater over catalysts containing these additional sites.

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