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Hydrogenation of Aromatic Hydrocarbons over Supported Pt Catalysts

I. Benzene Hydrogenation

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Vapor-phase benzene hydrogenation was studied over Pt dispersed on SiO_2, η-Al_2O_3, $SiO_2 \cdot Al_2O_3$, and TiO_2, as well as Pt powder. Activation energies and reaction orders were independent of the support as all E_{act} values fell between 10 and 13 kcal/mol and partial pressure dependencies were 0.6 ± 0.1 on H_2 and 0.1 ± 0.1 on benzene between 317 and 356 K. However, higher specific activities were obtained with acidic supports; for example, at 333 K under 50 torr benzene and 685 torr H_2, turnover frequencies increased from 0.015 s^{-1} on 0.78% Pt/η-Al_2O_3 and 0.033 s^{-1} on 0.96% Pt/SiO_2 to 0.072 on 0.24% Pt/$SiO_2 \cdot Al_2O_3$ and 0.078 on 0.95% Pt/TiO_2. An even larger increase occurred under 35 Torr benzene. This rate enhancement, which is similar to that found with Pd on these same supports, is associated with an additional contribution from benzene adsorbing on acidic sites on the support and reacting with spilled-over hydrogen. Significant inhibition and deactivation occurred under certain reaction conditions which altered steady-state activities. This is attributed to the concurrent formation of hydrogen-deficient surface species during benzene hydrogenation. © 1993 Academic Press, Inc.

INTRODUCTION

The use of acidic supports has been found to enhance benzene hydrogenation rates over dispersed Pd and, as a result, certain types of metal–support interactions (MSI) have been proposed to play an important role in this reaction (*1–3*). Enhancement of specific activity in the Fischer–Tropsch reaction over Group VIII metals supported on certain reducible oxides such as TiO_2 is a well-known example of one type of metal–support interaction (*4*). The effect of acidity on the hydrogenation of aromatic compounds confirmed that nonreducible supports could also affect catalytic activity; however, the explanations have varied from those used for TiO_2-supported metals (*1–4*). Clearly, a better understanding of the effect of the support material on catalytic behavior is important and may provide guidance in choosing or designing a better catalyst for a specific reaction. Benzene hydrogenation is sensitive to the support used, but neither the role of the support in this reaction nor the reaction mechanism on the metal surface has been unequivocally determined. Previous studies with Pd catalysts in this laboratory produced a reaction model explaining the enhanced activity over catalysts using more acidic supports (*2, 3*). This model proposed that benzene adsorbed on acid sites in the metal–oxide interfacial region could react with hydrogen spilled-over from the metal surface; consequently, more acidic supports can give an additional contribution to the overall activity. In this study, supported Pt catalysts were examined not only to compare turnover frequencies with those on Pd, but also to see whether a similar support effect occurred and, if so, whether this reaction model could again provide a reasonable explanation.

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EXPERIMENTAL

All the supported platinum catalysts, except for Pt/SiO_2, were prepared by an incipient wetness method using H_2PtCl_6 (Aldrich, $99.995^+\%$) dissolved in doubly distilled, deionized water and the following support materials: η-Al_2O_3 (prepared by calcination of alumina β-trihydrate at 873 K, Exxon Research & Engineering Co., 245 m^2/g), $SiO_2 \cdot Al_2O_3$ (Davison grade 979, 13% Al_2O_3, 400 m^2/g), and TiO_2 (Degussa P25, 50 m^2/g). An ion-exchange method was used for loading $Pt(NH_3)_4Cl_2$ (Strem) on SiO_2 (Davison grade 57, 220 m^2/g, 60–100 mesh). All the support materials were calcined in dry air at 773 K for 2 h before impregnation, and the impregnated catalyst powders were dried at 393 K overnight and then stored in a desiccator for later use. Actual metal loadings were determined by DC Plasma Emission Spectroscopy. Pt powder (Johnson Matthey, Puratronic, $99.99^+\%$) was used without further treatment. Pretreatments of fresh catalysts were carried out in situ prior to either adsorption or kinetic measurements. Details of the pretreatments have been reported earlier (*5*); in brief, Pt powder, Pt/SiO_2, Pt/Al_2O_3, and $Pt/SiO_2 \cdot Al_2O_3$ were reduced at 723 K under flowing H_2 (1 atm) for 1 h and then either purged with He or evacuated at 673 K prior to their use, while Pt/TiO_2 was given either a low-temperature reduction (LTR) at 473 K for 2 h or a high-temperature reduction (HTR) at 773 K for 1 h and then either purged with He or evacuated at that temperature prior to its use.

Hydrogen adsorption was carried out in a stainless steel adsorption system with a base pressure of 10^{-7} Torr, and details of the system have been described previously (*6*). Adsorption isotherms were recorded at 300 K in the range 20–150 Torr using H_2 (MG Industries, UHP grade, $99.999^+\%$) which had been passed through a molecular sieve trap and an Oxytrap (Alltech Asso.). Irreversible uptakes were determined by the difference between two consecutive isotherms with a 30-min evacuation in between, and Pt dispersions were calculated by the ratio of the irreversible uptake to the total metal loading assuming an adsorption stoichiometry of $H_{ad}/Pt_s = 1$.

All kinetic studies were conducted in the vapor phase in a differential, packed-bed microreactor system described earlier (*7*). H_2 and He (MG Industries, UHP grade, $99.999^+\%$) were flowed through separate molecular sieve traps and Oxytraps (Alltech Asso.). The benzene (J. T. Baker Co., $99.994^+\%$) was degassed by freeze–thaw cycles in a glove bag purged with N_2, then stored under N_2 and fed into the preheating arm of the reactor with either a syringe pump (Sage Instr.) or a peristaltic pump (Rainin Instr.). Typically, a gas mixture containing benzene and H_2 (or H_2 + He) at atmospheric pressure and a total flowrate of 47 sccm was passed through a glass reactor containing ca. 40 mg catalyst, which was immersed in a fluidized sandbath (Techne, Inc.) to maintain reaction temperatures between 313 and 356 K. A period of 25 min on stream was allowed before any sample was taken, and a bracketing technique with pure flowing H_2 was used while changing reaction conditions to minimize deactivation of the catalyst (*7*). In the Arrhenius runs an ascending-temperature sequence was typically followed by a descending-temperature sequence in order to detect any deactivation during these measurements. The reactor effluent was analyzed with a Hewlett–Packard gas chromatograph (HP-5890 Series II) equipped with a 1,2,3-tris(cyanoethoxy) propane column. Maximum conversions were around 12% while typical conversions were below 5%, and mass transfer limitations were found to be negligible under these conditions. Partial pressure dependencies on benzene were usually measured at a constant H_2 pressure of 685 Torr while the dependencies on H_2 were determined at a constant benzene pressure of 50 Torr.

RESULTS

The H_2 chemisorption results in Table 1 show that all the supported Pt catalysts are

TABLE 1

Hydrogen Adsorption (μmol/g cat) at 300 K on Pt Catalysts

Catalyst	T_{red} (K)	Total uptake[a]	Reversible uptake[a]	Irreversible uptake	H_{irr}/Pt (%)	d[b] (nm)
0.24% $Pt/SiO_2 \cdot Al_2O_3$	448	11.6 ± 0.3	6.1 ± 0.1	5.5	90	1.2
	673	7.8 ± 0.2	4.2 ± 0.1	3.6	58	1.9
	723	6.4 ± 0.1	3.7 ± 0.4	2.7	44	2.6
0.09% Pt/TiO_2 (LTR)	473	4.0 ± 0.2	2.2 ± 0.2	1.9	80	1.4
0.09% Pt/TiO_2 (HTR)	773	Nil	Nil	Nil	—	—
0.95% Pt/TiO_2 (LTR)	473	30.9 ± 0.5	13.3 ± 0.4	17.7	73	1.5
0.95% Pt/TiO_2 (HTR)	773	2.0 ± 0.1	1.5 ± 0.2	0.5	2.1	—
0.96% Pt/SiO_2	723	32.6 ± 0.4	9.0 ± 0.1	23.6	96	1.2
0.78% Pt/Al_2O_3	723	29.2 ± 0.4	8.6 ± 0.2	20.5	103	1.1
Pt powder[c]	773	2.8	—	—	0.11	1000

[a] With 95% confidence limits.

[b] Calculated from d (nm) = $1.13/(H_{irr}/Pt)$.

[c] From Ref. (7).

highly dispersed, as defined by the irreversible H_{ad}/Pt ratio. The decrease in dispersion of $Pt/SiO_2 \cdot Al_2O_3$ is assumed to be due to sintering when these samples were reduced at higher temperatures; the effect of reduction temperature on the dispersion of $Pt/SiO_2 \cdot Al_2O_3$ has been discussed earlier (*8*). The much lower H_2 uptakes on the Pt/TiO_2 (HTR) samples showed that the SMSI state was induced; i.e., a TiO_x overlayer on the Pt surface existed which decreases H_2 adsorption (*4*).

The temperature effect on the activities of these Pt catalysts at reaction conditions of P_{Bz} = 35 Torr and P_{H_2} = 700 Torr is shown by the Arrhenius plots in Fig. 1, and the activities and activation energies are compared in Table 2. All the supported catalysts were found to have a similar activation energy of 10–13 kcal/mol for benzene (Bz) hydrogenation, which is approximately the same as that found previously for this reaction over supported Pd catalysts (*2*) and for toluene hydrogenation on Pt and Pd catalysts (*9*, *10*). The specific activity, i.e., the turnover frequency, was calculated based on the H_{ad}/Pt ratio and it shows the following trend with respect to the support: $Pt/SiO_2 \cdot Al_2O_3$ > Pt/TiO_2 > Pt/SiO_2 > Pt/Al_2O_3, which is similar to that found for benzene and toluene hydrogenation over Pd catalysts (*2*, *10*). This implies that a similar activity contribution from certain supports

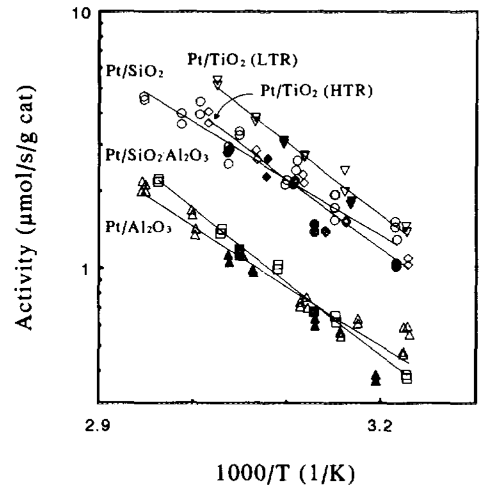

FIG. 1. Arrhenius plots of benzene hydrogenation over Pt catalysts at P_{Bz} = 35 Torr and P_{H_2} = 700 Torr: 0.78% Pt/Al_2O_3 (△, ▲), 0.24% $Pt/SiO_2 \cdot Al_2O_3$ (□, ■), 0.96% Pt/SiO_2 (○, ●), 0.95% Pt/TiO_2 (LTR) (▽, ▼), and 0.95% Pt/TiO_2 (HTR) (◇, ◆). Open symbols represent an ascending-temperature sequence and filled symbols represent a descending-temperature sequence.

TABLE 2

Kinetics of Benzene Hydrogenation over Pt Catalysts at P_{Bz} = 35 Torr and P_{H_2} = 700 Torr

Catalyst (sample)	$r_0 \times 10^{-6}$[a]	E_A[b] (kcal/mol)	Activity at 333 K	
			μmol/s/g cat	TOF ($s^{-1} \times 10^3$)
0.96% Pt/SiO_2 (I)	286	10.3 ± 1.5	3.40	72
0.96% Pt/SiO_2 (II)	303	11.7 ± 1.7	4.20	89
0.78% Pt/Al_2O_3 (I)	63.9	11.4 ± 1.6	1.45	36
0.78% Pt/Al_2O_3 (II)	63.9	11.4 ± 1.7	1.42	35
0.24% $Pt/SiO_2 \cdot Al_2O_3$[c]	863	13.0 ± 0.7	1.69	316
0.95% Pt/TiO_2 (LTR)	259	12.9 ± 1.3	5.85	168
0.95% Pt/TiO_2 (HTR)	746	12.4 ± 2.0	4.09	—
Pt Powder (I)	0.58	7.7 ± 0.7	3.71	658
Pt Powder (II)	0.57	7.8 ± 2.4	2.92	517
Pt Powder (III)	0.012	7.0 ± 0.3	0.21	36

[a] r_0 is defined as $r = r_0 \exp(E_A/RT)$, in μmol/s/g cat.

[b] With 95% confidence limits.

[c] Reduced at 723 K.

may occur. Although the measured activity of these supported catalysts was reproducible, that of the Pt powders varied by orders of magnitude among different samples, and Table 2 lists only three of the most active samples. Rapid deactivation, probably by the formation of carbonaceous residues, is considered to be the most likely cause of this irreproducible behavior for the Pt powders.

When conducted at P_{Bz} = 50 Torr and P_{H_2} = 685 Torr, Arrhenius plots gave somewhat different results, as indicated by Fig. 2 and Table 3. Again, the activation energy shows no dependence on the type of support, and it again falls between 10–13 kcal/mol, but the turnover frequencies show a somewhat different sequence because Pt/TiO_2 is now one of the most active catalysts, i.e., $Pt/TiO_2 \geq Pt/SiO_2 \cdot Al_2O_3 > Pt/SiO_2 > Pt/Al_2O_3$. The activity for each catalyst at this set of reaction conditions was found to be lower than those at 35 Torr Bz and 700 Torr H_2 for each catalyst; $Pt/SiO_2 \cdot Al_2O_3$ was most affected and its activity was about 20% that at the lower benzene pressure, whereas the other catalysts had about 50% of the former activity. From a general understanding that benzene hydrogenation is near zero order on benzene, the activity difference at these two partial pressure conditions should be very small, i.e., 5% at most; therefore, it is surprising that the small difference in reaction conditions caused such a signifi-

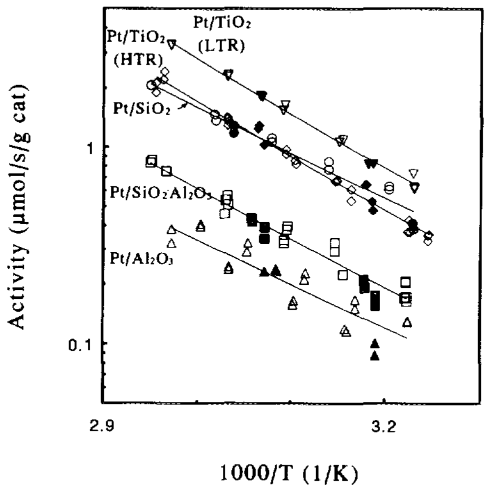

FIG. 2. Arrhenius plots of benzene hydrogenation over Pt catalysts at P_{Bz} = 50 Torr and P_{H_2} = 685 Torr: 0.78% Pt/Al_2O_3 (△, ▲), 0.24% $Pt/SiO_2 \cdot Al_2O_3$ (□, ■), 0.96% Pt/SiO_2 (○, ●), 0.95% Pt/TiO_2 (LTR) (▽, ▼), and 0.95% Pt/TiO_2 (HTR) (◇, ◆). Open symbols represent an ascending-temperature sequence and filled symbols represent a descending-temperature sequence.

TABLE 3

Kinetics of Benzene Hydrogenation over Pt Catalysts at P_{Bz} = 50 torr and P_{H_2} = 685 torr

Catalyst (sample)	$r_0 \times 10^{-7}$[a]	E_A[b] (kcal/mol)	Activity at 333 K	
			μmol/s/g cat	TOF ($s^{-1} \times 10^3$)
0.96% Pt/SiO_2	3.69	11.2 ± 1.2	1.56	33
0.78% Pt/Al_2O_3 (I)	1.21	11.1 ± 2.1	0.62	15
0.78% Pt/Al_2O_3 (II)	3.33	11.8 ± 0.8	0.60	15
0.24% Pt/$SiO_2 \cdot Al_2O_3$ (I)[c]	2.12	12.0 ± 1.4	0.30	55
0.24% Pt/$SiO_2 \cdot Al_2O_3$ (II)[c]	0.17	10.1 ± 1.0	0.39	72
0.95% Pt/TiO_2 (LTR) (I)	550	12.7 ± 0.4	2.66	75
0.95% Pt/TiO_2 (LTR) (II)	546	12.6 ± 0.6	2.77	78
0.95% Pt/TiO_2 (HTR) (I)	704	13.1 ± 1.1	1.81	—
0.95% Pt/TiO_2 (HTR) (II)	138	12.1 ± 0.6	1.56	—
0.95% Pt/TiO_2 (HTR) (II)[d]	138	11.7 ± 1.1	2.97	—

[a] r_0 is defined as $r = r_0 \exp(E_A/RT)$, in μmol/s/g cat.

[b] With 95% confidence limits.

[c] Reduced at 723 K.

[d] After 2nd pretreatment.

cant change in the activity of these supported Pt catalysts. As with the Pt powder, this variation is attributed to an inhibition or deactivation process. This complication has not been discussed in the literature, but it has been alluded to; for example, the recent paper by Flores *et al.* mentioned deactivation of 10–15% during a 2-h run (*11*). We believe this deactivation is the most likely reason for the wide scatter in the literature data and will be discussed later. No activity over the Pt powders was measurable at this set of reaction conditions, presumably due to this rapid deactivation.

A close examination of Figs. 1 and 2 reveals that the measured activities of Pt/SiO_2 and Pt/Al_2O_3 in the descending-temperature sequence are somewhat lower than that in the ascending-temperature sequence, and this results in slightly different activation energies. The effect of possible deactivation was further examined by long ascending-descending temperature sequences with Pt/SiO_2 at both partial pressure conditions, as shown in Fig. 3. These results show that only a minor extent of deactivation exists with this catalyst, and it is not sufficient to explain the two levels of activity found at the two different partial pressures, that is, Table 2 versus Table 3.

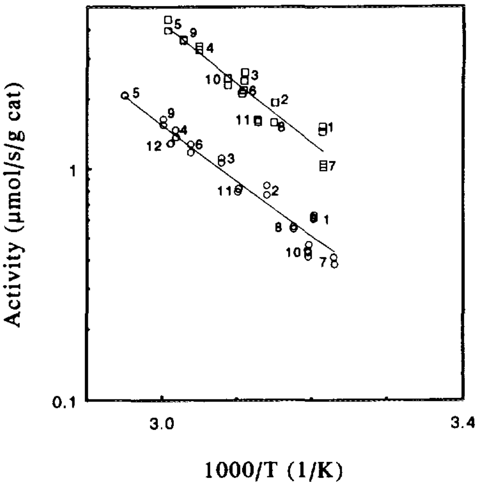

Fig. 3. Arrhenius plots of benzene hydrogenation over 0.96% Pt/SiO_2: P_{Bz} = 50 Torr and P_{H_2} = 685 Torr (○), and P_{Bz} = 35 Torr and P_{H_2} = 700 Torr (□); numbers next to the data points represent the sequence of measurement.

A series of tests in which the partial pres-

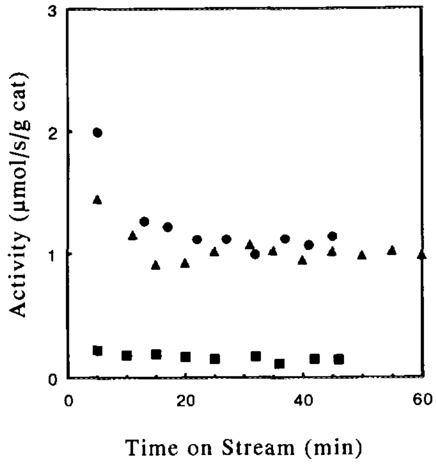

FIG. 4. Activity maintenance for benzene hydrogenation at 333 K over freshly reduced 0.24% $Pt/SiO_2 \cdot Al_2O_3$: P_{Bz} = 35 Torr and P_{H_2} = 700 Torr (●); a subsequent run at P_{Bz} = 50 Torr and P_{H_2} = 685 Torr (▲); and freshly reduced 0.24% $Pt/SiO_2 \cdot Al_2O_3$ at P_{Bz} = 50 Torr and P_{H_2} = 685 Torr (■).

sures were alternated between these two sets of reaction conditions was carried out to better understand the different activity levels that occurred. Figure 4 shows activity versus time on stream at both conditions; the activity seems to stabilize after about 20 min, which justifies out "steady-state" measurements after 25 min on stream. After a 30-min regeneration period in pure H_2 at 333 K following the first set of runs; the activity measured at 50 Torr Bz and 685 Torr H_2 changed little although the fraction of cyclohexane decreased because of the higher benzene concentration in the feed stream. However, when a freshly reduced catalyst was initially tested at 50 Torr Bz and 685 Torr H_2, the activity was much lower, and it remained low during a run at 35 Torr Bz and 700 Torr H_2 following this test and a subsequent run at these latter conditions after a H_2 treatment at 333 K. This result implies that the "steady-state" activity can depend on the initial reaction conditions, that the activity can stabilize quickly (less than 5–10 min), and that the stabilized activity may not be strongly affected by a later change of benzene partial pressure. Treatment at 333 K in 20% O_2, 80% He did not regenerate the catalyst, but the $Pt/SiO_2 \cdot Al_2O_3$ catalyst did recover its activity following calcination in 20% O_2 at 673 K and a subsequent standard reduction at 723 K.

A reversible maximum in activity versus temperature for benzene hydrogenation has been reported frequently, and it has been explained successfully by assuming a decrease in the surface coverage of benzene at higher temperature (*12*). The Pt/Al_2O_3 catalyst was tested over a wide temperature range to verify the existence of this reversible activity maximum, which was found to occur near 473 K at 50 Torr Bz and 685 Torr H_2, as shown in Fig. 5. At 35 Torr Bz and 700 Torr H_2 the conversion was approaching 100% at 413 K; consequently, any decrease could also be due to thermodynamic considerations. The two levels of activity at different reaction conditions are again obvious in Fig. 5, and the deactivation under 35 Torr Bz and 700 Torr H_2 is apparent at lower temperatures.

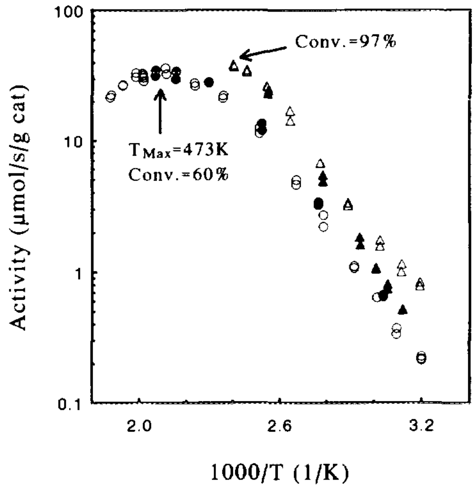

FIG. 5. Temperature effect on benzene hydrogenation over 0.78% Pt/Al_2O_3: P_{Bz} = 35 torr and P_{H_2} = 700 Torr (△, ▲), and P_{Bz} = 50 Torr and P_{H_2} = 685 Torr (○, ●). Open symbols represent an ascending-temperature sequence and filled symbols represent a descending-temperature sequence.

The partial pressure dependencies of

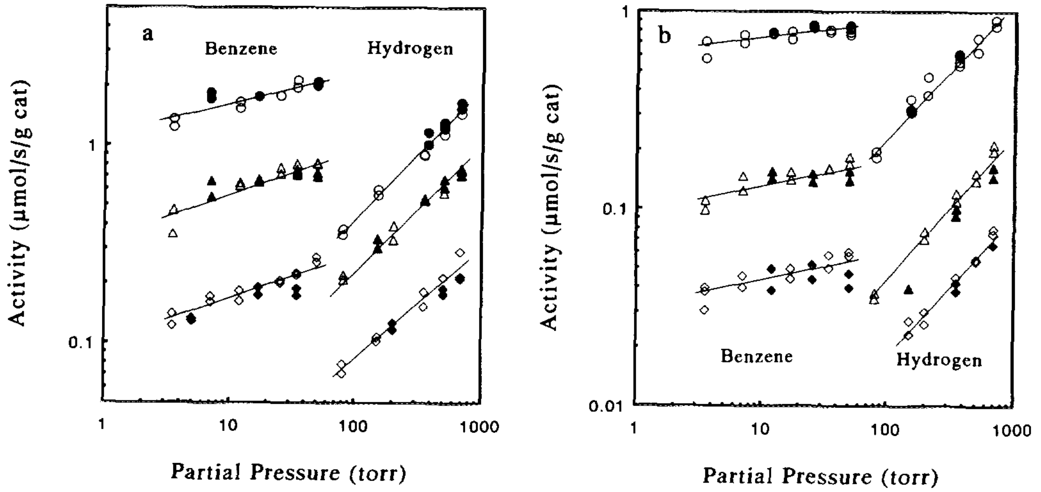

FIG. 6. Partial pressure dependencies of benzene hydrogenation over Pt at 317 K (◇, ◆), 337 K (△, ▲), and 356 K (○, ●): (a) 0.78% Pt/Al_2O_3 and (b) 0.24% $Pt/SiO_2 \cdot Al_2O_3$. Open symbols represent a decreasing-pressure sequence and filled symbols represent an increasing-pressure sequence. The H_2 dependency was measured at 50 Torr Bz, and the Bz dependency was measured at 685 Torr H_2.

these Pt catalysts on Bz were determined so that they could be directly compared to results of toluene hydrogenation on Pt (*9*) and benzene hydrogenation on Pd catalysts (*2*). The reaction order of Bz was determined at a constant H_2 pressure of 685 Torr, and the reaction order on H_2 was determined at a constant Bz pressure of 50 Torr. Two sets of results are given in Fig. 6; the remainder are shown elsewhere (*13*). A slightly positive reaction order on benzene occurs at all three temperatures, while the reaction order on H_2 was somewhat above one-half. Similar behavior was observed with all the catalysts, as shown in Fig. 7, and between 313 and 363 K the Bz reaction order was 0.1 ± 0.1, while the H_2 reaction order remained 0.6 ± 0.1. The support had no significant effect on reaction orders.

DISCUSSION

Based on numerous UHV (ultra-high vacuum) studies of benzene on Pt(111) (*14–31*), Pt(100) (*19, 20, 32, 33*), and Pt(110) (*34–36*), the interaction of benzene with a Pt surface is generally assumed to adsorb by a π-bond interaction in which the ring lies parallel to the metal surface. Benzene adsorption exhibits no preference among these three low-index planes because the work function change upon saturated adsorption (*15, 19, 33, 35*), the saturation surface coverage (*16, 18, 33, 35*), and the EELS spectra of ad-

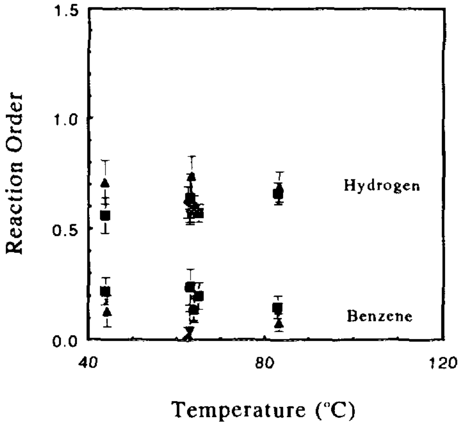

FIG. 7. Reaction orders for benzene hydrogenation over Pt catalysts: 0.78% Pt/Al_2O_3 (■), 0.96% Pt/SiO_2 (●), 0.95% Pt/TiO_2 (LTR) (◆), 0.95% Pt/TiO_2 (HTR) (▼), and 0.24% $Pt/SiO_2 \cdot Al_2O_3$ (▲). The H_2 dependency was measured at 50 Torr Bz, and the Bz dependency was measured at 685 Torr H_2. The error bars represent 95% confidence limits.

sorbed species (*18*, *25*, *34–36*) are similar for each crystal surface. In addition to these three single-crystal Pt surfaces, the vibrational spectrum from neutron inelastic spectroscopy of benzene adsorbed on Raney Pt (*37*) is very similar to the EELS spectrum of benzene on Pt(111) (*18*, *25*), and TPD (temperature-programmed desorption) results with a Pt 6(111) × (111) surface differed little from those with Pt(111) (*23*). All these observations allow the conclusion that benzene adsorption on Pt is essentially indifferent to the kink, step, or edge site distributions, and these findings are consistent with the general understanding that benzene hydrogenation is a structure-insensitive reaction (*38*). Benzene adsorbs primarily in a molecular form, as Tsai and Muetterties showed that around 90% of the benzene adsorbed on Pt(111) could be removed reversibly (*23*). However, TPD studies of benzene adsorbed on Pt have shown that at low coverage benzene desorbs around 500 K, but at higher coverage a second desorption peak appears around 320–400 K (*15*, *16*, *18*, *21–23*, *27*, *30*), and some H_2 evolution occurs above 400 K (*15*, *23*, *27*). This implies that a dehydrogenation process can also occur on Pt surfaces.

Benzene adsorption on oxide surfaces has also been reported in the literature (*39–49*), and it has been proposed to occur via an interaction with either cation sites, such as exchanged metal cations in a zeolite or exposed Al^{+3} cations on Al_2O_3, or surface hydroxyl groups (*41*, *48*, *49*). Based on UV and IR spectra, Primet *et al.* have proposed that benzene adsorption strength follows the sequence: CaY > LY > HY < $SiO_2 \cdot Al_2O_3 \geq Al_2O_3 > SiO_2$ because they found that evacuation at room temperature removed adsorbed benzene from SiO_2 whereas 323 K was needed for Al_2O_3 and $SiO_2 \cdot Al_2O_3$ and 423 K was necessary for zeolites (*40*). Since their samples were calcined and evacuated at 773 K, their findings suggest that the strength of benzene adsorption on Lewis acid sites increases as the acidity of the oxide surface increases.

Benzene adsorbed on an oxide surface appears to have a π-bond interaction similar to that on a metal (Pt) surface because Fischer *et al.* have reported that benzene lies with the ring parallel to the substrate surface (*43*); however, the bond strength is probably lower. Szilágyi has found that benzene adsorption on SiO_2 and Pt/SiO_2 showed very similar IR adsorption bands (*50*), and NMR studies have shown that benzene adsorbed on both Al_2O_3 and Pt/Al_2O_3 showed similar surface motion, i.e., a fast rotation around the hexagonal symmetric axis normal to the surface, libration, and translation, but the motion on Pt/Al_2O_3 was somewhat more restricted than on Al_2O_3 (*51–54*). It has been estimated that the BET monolayer coverage of Bz on Al_2O_3 at 300 K is 1.4 molecule nm^{-2} (*54*), while on TiO_2 (rutile) at 288 K it is 1.8 molecule nm^{-2} (*43*, *44*); both densities are only slightly lower than that reported on Pt (111) (*16*, *18*, *27*). Although consideration of the Kelvin equation showed that pore condensation may have occurred during these adsorption studies, the similar surface concentrations imply that on either metal or oxide surfaces weak, rather than strong, chemisorption predominates, because most of the benzene adsorbed on either surface can be removed by evacuation at relatively low temperatures (*23*, *40*). Thus, one can assume that benzene adsorption on a Pt surface differs little from that on an oxide surface although the bond strength may be somewhat higher on Pt.

A comparison of results from this study and those from a previous investigation of Pd catalysts (*2*) shows that the kinetic behavior of benzene hydrogenation is very similar on Pt and Pd catalysts although the TOF is significantly higher on Pt, as indicated in Table 4. In both systems the apparent activation energy falls between 10 and 13 kcal/mol, the apparent reaction order on H_2 between 313–363 K is typically 0.6 ± 0.1, and the apparent reaction order on benzene over this temperature range is near zero but slightly positive. Both metals show a reversible maximum in activity at elevated temper-

TABLE 4

Comparison of Benzene Hydrogenation Activity over Supported Pt and Pd Catalysts

Catalyst	T_{red} (K)	$\frac{H_{ad}}{Metal}$	Activity at 373 K[a]		
			$\frac{\mu mol}{s \cdot g\ metal}$	TOF ($s^{-1} \times 10^3$)	$\frac{TOF_{Pt}}{TOF_{Pd}}$
1.71% Pd/SiO_2	673	0.36	8	14	—
0.96% Pt/SiO_2	723	0.96	1001	207	15
			(2401)	(487)	(35)
1.80% Pd/Al_2O_3	673	0.48	62	18	—
0.78% Pt/Al_2O_3	723	1.03	499	96	5
			(1180)	(225)	(12)
1.95% $Pd/SiO_2 \cdot Al_2O_3$	448	0.56	428	174	
1.95% $Pd/SiO_2 \cdot Al_2O_3$	673	0.41	85	36	—
0.24% $Pt/SiO_2 \cdot Al_2O_3$	723	0.44	861	377	10
			(5838)	(2598)	(72)
2.03% Pd/TiO_2 (LTR)	448	0.60	183	93	—
0.95% Pt/TiO_2 (LTR)	473	0.73	2221	594	6
			(5032)	(1359)	(15)
2.03% Pd/TiO_2 (HTR)	673	0.44	13	22	—
0.95% Pt/TiO_2 (HTR)	773	0.02	1613	432[b]	20
			(3163)	(854[b])	(39)

[a] Determined at 50 Torr Bz and 685 Torr H_2; values for Pd are from Ref. (*2*). The numbers in parentheses represent the activity at 35 Torr Bz and 700 Torr H_2.

[b] TOF based on the H_{ad}/Pt value for Pt/TiO_2 reduced at 473 K.

atures, with the maximum occurring on Pt at 473 K rather than at 495 K on Pd. The influence of the support on the catalytic performance is also similar with both Pt and Pd catalysts. In both families of catalysts, the support had little or no effect on either the apparent activation energy or the reaction orders on benzene and hydrogen; however, with either metal the turnover frequency was found to be higher when a more acidic support was used. Similar enhancements from acidic supports have been reported earlier with Pd catalysts (*1*, *2*). The similarity in kinetic parameters suggests that a common reaction mechanism may exist on Pt and Pd catalysts; however, the TOF on Pt is 5–20 times higher than that on Pd, as shown in Table 4. This is due to the intrinsic differences between these two metals, as unsupported Pt has been reported previously to be more active than Pd in this reaction (*55*). Consequently, the relative contribution of an acidic support is noticeably less pronounced with Pt and with Pd.

We have preferred to explain this increase in the specific activity of Pd when it is dispersed on acidic supports by an additional activity contribution from the metal–support interfacial region, in which a reaction between spilled-over hydrogen and benzene adsorbed on acid sites on the oxide surface enhances the overall reaction (*2*). Although electron-deficient Pd particles have also been proposed to explain the higher activity on acidic supports (*1*), no evidence was provided to substantiate this claim; furthermore, the large Pd crystallites (3–9 nm) in our catalysts disallowed the possibility of an electronic effect (*3*, *10*). In addition, Pt clusters in a zeolite which appear to be electron deficient have a turnover number that is smaller by one-half compared to that of small Pt crystallites on the same zeolite (*56*). The previously mentioned similarities in kinetic parameters and support effects suggest that this same model may be applicable to these Pt catalysts even though we cannot discount the possibility of an electronic effect due to the very small Pt particles (1–2 nm) in these catalysts. As discussed, benzene adsorbs on oxide surfaces via a π-bond interaction with metal cation sites or surface hydroxyl groups (*39–49*), but benzene hydrogenation rates over pure oxides are very low and are negligible at our reaction conditions (*2*, *10*, *57*, *58*); for example, no benzene hydrogenation activity occurred on HCl-impregnated TiO_2 up to 433 K (*2*), no toluene hydrogenation activity existed on HCl-impregnated $SiO_2 \cdot Al_2O_3$ or TiO_2 (*10*), SiO_2 and η-Al_2O_3 had no activity for benzene hydrogenation up to 400 K (*57*, *58*), and a decationized zeolite was active only above 620 K (*59*). Deuterium exchange with benzene is possible on oxides, even at room temperature (*60–62*), but the absence of benzene hydrogenation on these oxide surfaces indicates that hydrogen exchange occurs by a different and more facile mechanism than the addition of hydrogen to break the aromatic resonance. Therefore, active H species have to be present to make possible any hydrogenation activity in the metal–support interfacial region, and this requirement can be fulfilled by hydrogen spilled over from the metal surface (*63*).

Spilled-over hydrogen has been found to be not only active for hydrogenation reactions on oxide surfaces, but also capable of creating active sites on certain oxide surfaces (*63*), and Teichner and co-workers have reported that benzene reacts readily with spilled-over hydrogen on oxide surfaces at 443 K (*64*, *65*). Although Antonucci *et al.* and Ceckiewicz and Delmon found that mixing Pt/Al_2O_3 with pure Al_2O_3 increased the specific benzene hydrogenation activity (based on Pt) by as much as fourfold (*57*, *66*), Figueras *et al.* and Flores *et al.* did not find such an activity enhancement (*1*, *11*). These experiments are complicated by the possibility that the Al_2O_3 in the mixture acts as a scavenger of impurities that can poison the catalyst (*66*). Antonucci *et al.* also found that the activation energy of 9.2 kcal/mol for benzene hydrogenation was the same for the Pt/Al_2O_3 catalyst and its mixture with Al_2O_3 (*57*). These investigations provide additional support for our reaction model. Primet *et al.* examined the hydrogenation of benzene adsorbed on a Pt/zeolite after removal of gas-phase benzene and suggested that the benzene migrates to the Pt where hydrogenation occurs (*67*). This cannot account for higher activity under our steady-state conditions, however, because the Pt surface is nearly saturated with benzene. Finally, although adsorbate-induced surface reconstruction of the metal particles may be possible, as proposed for small Pt aggregates in a Y zeolite, for example (*68*), we do not consider this a likely explanation in this case because this reaction is structure-insensitive and benzene adsorption on the Pt(111), (100), and (110) surfaces is very similar.

Although the mechanistic details of the reaction between spilled-over hydrogen and adsorbed benzene are not known at this time, a unifying reaction scheme for hydrogenation of aromatic molecules over dispersed noble metal catalysts can be obtained if a common reaction mechanism and a common role of the support are assumed. An effort to provide a single, universal reaction model will be made here. A large number of different reaction sequences were examined in detail, and only one general model gave reasonable fitting parameters (*13*). Evidence exists that acid sites on the oxide, especially Brønsted sites, act as adsorption sites for benzene and, if activated hydrogen is available, they can contribute to the activity (*2*, *10*). The pretreatment given the catalyst can alter the ratio of Brønsted-to-Lewis acid sites on SiO_2–Al_2O_3, for example, because higher temperatures can transform the former to the latter. However, in a recent IR study of the Pt/SO_4^{2-}–ZrO_2 system, Ebitani *et al.* reported that hydrogen spillover from Pt can transfer electrons to Lewis acid sites and form protons, i.e., Brønsted acid sites, on oxide surfaces (*69*). By analogy with the acid-catalyzed hydrogenation of benzene reported in homogeneous systems (*70*, *71*), the formation of a carbonium ion from the interaction between benzene and a Brønsted acid site seems reasonable, and it could represent one route for hydrogenation on acidic surfaces. This possibility has been previously suggested (*56*). Since $SiO_2 \cdot Al_2O_3$ and TiO_2 have been reported to possess strong Lewis acid sites (*72*, *73*) as well as Brønsted acid sites, and since $Pt/SiO_2 \cdot Al_2O_3$ and Pt/TiO_2 have the highest specific activity for benzene (and toluene) hydrogenation, we hypothesize 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 spillover-hydrogen. This hypothesis provides an explanation of the effect of support acidity, but it must be studied further because the effect of treatment temperature and the influence of residual chloride make it a complex system.

Many studies of vapor-phase benzene hydrogenation over Pt catalysts have been conducted (*55–58*, *67*, *74–109*) and activities and kinetic parameters are tabulated elsewhere (*12*, *13*); however, a summary of these results is given here. Most of the activation energies for supported Pt are within or near the range reported in Tables 2 and 3, i.e., 9–13 kcal/mole, although high and low values of 17.9 and 2.3 kcal/mol have been reported. The lower values of 7–8 kcal/mol found for our Pt powder catalysts are consistent with previously reported low values (typically 7–10 kcal/mol) for unsupported Pt. Despite the consistency of apparent activation energies, turnover frequency (TOF) values extrapolated to 333 K and a total pressure of 1 atm vary by almost two orders of magnitude for the supported catalysts ($1–79 \times 10^{-2}\ s^{-1}$) and even more if unsupported Pt is included. It is surprising that no good agreement exists among these literature data because it is generally accepted that this reaction is structure-insensitive. With no exceptions, the benzene reaction order has been reported to be zero order, while the H_2 reaction order has varied from 0.4 to 1.0. These studies have ranged from 298 to 423 K; however, it is remarkable that no previous investigation has determined how these two reaction orders vary with temperature. Our partial pressure dependencies are very consistent with these results, and the significance of their dependence on temperature will be addressed in a subsequent paper in which a reaction model is proposed and fitted to these data (*110*).

The two levels of activity found in this study, which seem to be dependent on initial partial pressures, could be associated with the cause of the wide variation of TOF values. There appear to be some uncontrolled parameters; for example, the formation of H-deficient carbonaceous species on Pt mentioned earlier is one possibility and impurities in the feed stream is another. A careful examination of the reaction models proposed for this reaction revealed not only that the hypothesis of H-deficient species on the Pt surface produced by a concurrent surface decomposition reaction was essential, but also that these H-deficient species can predominate on the surface (*13*, *110*). Furthermore, a good fit could be obtained assuming that only one H-deficient species was dominant, but this particular species had to be the phenyl group, C_6H_5 (*13*, *110*). Phenyl species from benzene adsorption on Pt surfaces have not been reported in the literature, but they have been identified on Ag(111) (*111*), Os(0001) (*112*), and Ni(111) (*113*). In addition, molecular hydrogen has been desorbed from Pt surfaces during benzene TPD experiments (*15*, *23*, *27*); consequently, strong evidence exists that benzene adsorbed on Pt can form H-deficient species. In their study of benzene adsorption and hydrogenation using a pulse-type reactor, Orozco and Webb detected an unusually large amount of benzene (or toluene) retained on Pt/SiO_2 and Pt/Al_2O_3 which was inactive and not removable by H_2 up to 523 K, and a post analysis found carbonaceous residues on these Pt samples (*82*). These observations are consistent with both the proposal here that carbonaceous species are formed on Pt catalysts under reaction conditions and the observation that H_2 reduction at 723 K alone was not able to regenerate our low-activity catalysts. Campbell *et al.* estimated 55% of the benzene monolayer on Pt(111) dehydrogenated to liberate H_2 during heating to over 450 K, based on a detailed study combining TPD, AES and XPS (*27*). This indicates that the surface coverage of H-deficient species can be high, consistent with our assumption that the most abundant surface species are H-deficient species; however, the reaction temperatures in our study were typically below 350 K, a region in which Campbell *et al.* assumed only molecularly adsorbed benzene occurred (*27*). Nevertheless, we wish to emphasize that the existence of H-deficient carbonaceous species not only is required to explain the kinetic parameters in our rate equation (*13*, *110*), but also can explain the wide range of specific activity reported in the literature. This proposal has not been made previously for Pt catalysts although it has been suggested for Pd surfaces (*3*). The point we wish to emphasize is that the initial reaction conditions appear to be extremely important in rapidly establishing the activity of the Pt surface which is maintained under subsequent steady-state conditions.

Benzene hydrogenation is typically considered as a structure-insensitive reaction on Pt because, within a given investigation, the turnover frequency has been found to be relatively independent of the metal dispersion (*11*, *56*, *58*, *85*, *106*, *114*), the type of metal precursor (*85*, *105*), the residual Cl content (*11*, *85*), and the pore structure of the support (*58*, *85*). In other words, with a single support in a given laboratory, evidence for a structure-insensitive reaction can be obtained. A small decrease in the activity of Pt after alloying with small amounts of a low-activity metal, such as Zr (*103*), Au (*109*), or Cu (*115*), has been interpreted as evidence of structure sensitivity because an electronic effect was excluded by XPS experiments (*109*); however, the observed changes were small, i.e., a factor of 2. Both one-atom-thick metal rafts and atomically dispersed metal atoms as well as very small crystallites would be defined as 100% dispersion, but whether the former surface structure is favored for benzene hydrogenation is uncertain at this moment. Campbell *et al.* studied the effect of deposited Bi on benzene adsorption on a Pt(111) single crystal and concluded that reducing the Pt ensemble size first inhibited the dehydrogenation reaction and then lowered the benzene desorption temperature (*27*). As larger ensembles exist on large Pt crystallites, particularly those associated with the (111) plane, this could explain the more rapid deactivation of the Pt powder observed in this study and the greater variation in activity with initial reaction conditions. Based on the results of Campbell *et al.* (*27*), low Bi coverages would hinder benzene dehydrogenation and decrease H-deficient species, thus increasing activity, whereas at high Bi coverages benzene adsorption itself could be decreased thus resulting in suppressed activity. This prediction is consistent with the two maxima in the activity versus metal composition observed with a series of Pt–Re/Al_2O_3 catalysts (*75*). Although structure sensitivity in the benzene hydrogenation reaction has not been established, the possibility exists that the dehydrogenation/decomposition of benzene on Pt may be structure-sensitive. Consequently, the final activity based on the remaining free metal surface area could vary significantly.

SUMMARY

Benzene hydrogenation was studied over Pt dispersed on SiO_2, η-Al_2O_3, $SiO_2 \cdot Al_2O_3$, and TiO_2 as well as Pt powder. The kinetic parameters were very similar to those for Pd catalysts, i.e., the activation energy and the apparent reaction orders on H_2 and benzene were essentially independent of the support, all activation energies fell between 10–13 kcal/mol, and the apparent reaction orders were 0.6 ± 0.1 on H_2 and 0.1 ± 0.1

on benzene between 317 and 356 K. However, the support was found to affect the specific activity, which was higher with acidic supports. The steady-state benzene hydrogenation activity seemed to be sensitive to the initial set of reaction conditions, and the turnover frequency decreased by 80% on $Pt/SiO_2 \cdot Al_2O_3$ when the initial partial pressures were changed from 35 Torr Bz and 700 Torr H_2 to 50 Torr Bz and 685 Torr H_2. Inhibition due to a H-deficient species formed from a concurrent surface decomposition reaction is proposed to explain this observation. The similar trends in catalytic performance of these Pt catalysts compared to those of Pd catalysts from previous studies suggest that the model previously proposed for Pd is again applicable. This model attributes the enhanced activity obtained with acidic supports to an additional contribution from the metal–support interfacial region in which the benzene adsorbs on acid sites and reacts with hydrogen migrating from the metal surface, and it provides an unified scheme for noble metals dispersed on these oxide supports. Regardless, the benzene hydrogenation reaction appears to be complicated by surface decomposition reactions, pretreatment effects, and residual chloride levels, and further study is necessary to elucidate these parameters.

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