

# Competitive Hydrogenation of Benzene and Toluene on Palladium and Platinum Catalysts

Deepak Poondi and M. Albert Vannice<sup>1</sup>

Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802-4400

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This study examines the influence of the support on the relative hydrogenation rates of benzene and toluene in mixtures, and it also analyzes the influence of the chosen reaction model on the interpretation of fitted rate parameters. The relative hydrogenation rates,  $R_{T/B}$ , over Pd catalysts at an equimolar feed composition of 50% toluene and 50% benzene were  $0.65 \pm 0.10$  and had little dependence on the support, the pretreatment temperature, or the reaction temperature. A supported Pt catalyst was also studied, and the threefold higher  $R_{T/B}$  value for Pt indicates that toluene hydrogenation was more favored over Pt compared to Pd. The variations in the ratio of adsorption equilibrium constants,  $K_{T/B}$ , which have been attributed previously to changes in the electron deficiency of the metal based on a simple dual-site kinetic model, have been re-examined. Some internal inconsistencies which existed when the kinetic parameters were evaluated at different reaction temperatures were removed when a more comprehensive model invoking formation of hydrogen-deficient surface species was utilized. These apparent  $K_{T/B}$  ratios can include additional kinetic dehydrogenation parameters, and analysis of the results with the latter model revealed that these  $K_{T/B}$  ratios can also reflect the relative formation of hydrogen-deficient species like phenyl or tolyl groups. Consequently, the assumption that variations in  $K_{T/B}$  values represent only changes in relative adsorbate bond strength must be viewed with caution because the propensity of the metal surface to form hydrogen-deficient surface species under reaction conditions may also alter these ratios. © 1996 Academic Press, Inc.

## INTRODUCTION

Enhanced activities have been reported for hydrogenation of benzene, toluene, and xylenes over Pd and Pt catalysts supported on acidic oxides (1–5). Originally, Figueras *et al.* attributed the higher activity of benzene on acidic supports to the presence of electron-deficient Pd (1), and Massardier *et al.* have also postulated the presence of electron-deficient metal to explain their results for hydrogenation of benzene–toluene mixtures on Pt catalysts (9). Although this latter explanation could be applicable to small metal clus-

ters in a zeolitic framework, it is much more difficult to apply it to larger (2–4 nm) metal crystallites whose electronic properties are expected to be similar to those of bulk metal; consequently, explanations for this behavior have varied. Another explanation for the enhanced activities with Pd and Pt dispersed on acidic supports involves a Langmuir–Hinshelwood model which invokes one set of sites on the metal and another set on the support (6–8). An enhanced rate of isomerization of *o*-xylene to *m*-xylene over acidic supports helped to confirm the assumption that Brønsted acid sites were present on these oxide surfaces and to support the proposal that hydrogen adsorbs dissociatively on the metal and spills over onto the support where it reacts with the adsorbed aromatic hydrocarbon.

Rahaman and Vannice found that when the most acidic silica–alumina was used as a support, the largest activity enhancement over Pd occurred for benzene hydrogenation and smaller increases in activity were obtained for toluene and xylene hydrogenation (3). Application of the dual-site model implied that the greatest contribution from the acid sites on the support occurred during benzene hydrogenation; therefore, the possibility existed that the selectivity during hydrogenation of benzene–toluene mixtures might be altered by the appropriate choice of support. Significant changes in activity and selectivity, which were attributed to the electron-deficient nature of the metal, have been reported for competitive hydrogenation of toluene and benzene on different acidic zeolite-supported Pt catalysts (9). Because of the significant differences in activity obtained with Pd dispersed on nonzeolite oxides, a similar study for Pd seemed appropriate to determine if such changes also occurred and to see which model was most appropriate. Furthermore, analysis of the reaction kinetic parameters for these concurrent reactions in the manner forwarded by Massardier and co-workers could provide additional insight into the surface chemistry, especially when determined at different temperatures. However, it is important to examine the effect of the chosen reaction model on the observed rate parameters because the interpretations associated with these parameters can be altered markedly. The results of these efforts are presented here.

<sup>1</sup> To whom correspondence should be addressed.

## EXPERIMENTAL

The supported catalysts used in this study were made by incipient wetness and ion-exchange techniques using  $\eta$ -Al<sub>2</sub>O<sub>3</sub> prepared from aluminum  $\beta$ -trihydrate (Exxon Research and Engineering Company), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Davison Grade 979), PdCl<sub>2</sub> (Alfa products), and (NH<sub>3</sub>)<sub>2</sub>Pd(NO<sub>2</sub>)<sub>2</sub> (Alfa), as described previously (2, 3). All supports were calcined in flowing air for 2 h at 773 K prior to impregnation. A commercial 3.61% Pd/C catalyst (Engelhard Corporation) was also studied. The catalysts were dried in an oven at 393 K for at least 16 h and then stored in a desiccator. The Pt/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst was one that had been prepared previously in our laboratory by an incipient wetness technique using an aqueous solution of chloroplatinic acid (4).

Two different pretreatment procedures were utilized. Pretreatment A involved heating the catalyst in flowing He to 393 K, holding for 30–60 min, and then reducing in flowing H<sub>2</sub> for 1 h at the desired temperature. Pretreatment B utilized a calcination step in 20% O<sub>2</sub>/80% He at 573 K for 2 h followed by cooling to 448 K in flowing He and then reducing in flowing H<sub>2</sub> at 448 K or 573 K for 1 h.

Both fresh and used catalyst samples were characterized by hydrogen chemisorption in a UHV adsorption system described earlier (8) following the same pretreatment as that used in the kinetic runs. The dual isotherm technique described by Boudart and co-workers was used to obtain irreversible chemisorption on Pd (10, 11), and a 1/1 ratio for H<sub>ad</sub>/Pd<sub>s</sub>, where Pd<sub>s</sub> is a surface atom, was assumed to calculate the Pd dispersion,  $D = \text{Pd}_s/\text{Pd}_{\text{total}}$ . From these  $D$  values average Pd crystallite sizes,  $d$ , were determined from the relationship  $d(\text{nm}) = \frac{1.13}{D}$ .

Benzene and toluene (Aldrich HPLC grade, 99.9+%) were used for the kinetic runs after carrying out freeze–

thaw cycles under N<sub>2</sub> on each of the aromatics to remove dissolved air. The two aromatics were mixed in a N<sub>2</sub>-purged glove bag to achieve the desired composition. Hydrogen (99.999%, MG Ind.) and helium (99.999%, Linde) were further purified by flowing through Oxytraps (Alltech Assoc.). The differential reactor usually contained 0.20–0.25 g catalyst, and a Sage syringe pump was used to introduce the liquid feed into a preheated section maintained at 423 K. Aromatic condensation was eliminated by keeping the partial pressures of the aromatics low and the line temperatures well above the boiling points of the aromatic hydrocarbons. Further details are given elsewhere (12). A bracketing technique was employed in the kinetic runs. The reaction was allowed to reach steady state during a 25-min period, sampling was done over a 10- to 15-min period, and then the sample was kept under pure flowing hydrogen for 25 min while conditions were changed and before the hydrocarbon feed was again introduced. All kinetic runs were carried out under isothermal conditions. The effluent gas was analyzed using a gas chromatograph (H-P Model 5890 Series II) which was fitted with a TC detector, and an electronic integrator (H-P Model 3394A) was used to determine peak areas. A 1,2,3-tris(2-cyanoethoxy) propane column was used to separate the components in the product gas.

Competitive hydrogenation of benzene and toluene was carried out at a total aromatic partial pressure near 50 Torr and a hydrogen partial pressure of 680 Torr. Conversions were kept below 15% and care was taken to ensure that all catalysts satisfied the Weisz criteria to avoid any mass transfer limitations (13). At least three benzene–toluene mixtures were used to evaluate the kinetic parameters for each catalyst. Bracketing each benzene–toluene mixture run by one with a pure benzene feed proved helpful because it monitored any deactivation if it occurred.

TABLE 1

H<sub>2</sub> Adsorption on Fresh Pd and Pt Catalysts

Catalyst	$T_r^a$ (K)	H <sub>2</sub> uptake ( $\mu$ moles/g)		$D$ [H <sub>irrev</sub> /Pd <sub>total</sub> ]	$d$ (nm)	H <sub>rev</sub> /Pd <sub>b</sub>
		Reversible	Irreversible			
1.67% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	673	32.5	32.5	0.41	2.7	0.70
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	42.5	37.5	0.49	2.3	1.1
0.22% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	3.5	5.0	0.48	2.3	0.65
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	573	8.3	7.3	0.26	4.3	0.42
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	573	6.0	7.8	0.28	4.0	0.28
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	3.8	5.0	0.18	6.3	0.16
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	673	32.5	20	0.26	4.4	0.57
3.61% Pd/C	573	82	30	0.18	8.7 (3.8) <sup>c</sup>	0.59
0.78% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	723	9.0	13.0	1.1 <sup>d</sup>	1.1	—

<sup>a</sup> Pretreatment A, reduction temperature.

<sup>b</sup> Pretreatment B, calcined.

<sup>c</sup> From Ref. (52), number in parentheses based on TEM.

<sup>d</sup> Total uptake.

TABLE 2  
Hydrogen Chemisorption on Used and Regenerated Pd and Pt Catalysts

Catalyst	$T_r$ (K)	$H_2$ uptake ( $\mu$ moles/g)		$D$ [ $H_{irrev}/Pd_{total}$ ]	$d$ (nm)	$H_{rev}/Pd_b$
		Reversible	Irreversible			
1.67% Pd/ $\eta$ - $Al_2O_3^a$	673	33.8	3.8	0.047	23.7 <sup>b</sup>	0.45
1.67% Pd/ $\eta$ - $Al_2O_3^c$	673	32.5	15.0	0.19	5.9	0.51
1.67% Pd/ $\eta$ - $Al_2O_3^d$	673	32.5	15.0	0.19	5.9	0.51
1.64% Pd/ $SiO_2$ - $Al_2O_3^a$	448	35.0	21.3	0.28	4.1 <sup>b</sup>	0.62
1.64% Pd/ $SiO_2$ - $Al_2O_3^c$	448	32.5	30.0	0.39	2.9	0.69
1.64% Pd/ $SiO_2$ - $Al_2O_3^d$	448	32.5	29.5	0.38	3.0	0.68
0.78% Pt/ $\eta$ - $Al_2O_3$	723	12.5	8.0	1.03	1.1 <sup>e</sup>	—

<sup>a</sup> Deactivated samples.

<sup>b</sup> Apparent crystallite size.

<sup>c</sup> Deactivated sample after one regeneration in  $O_2$ .

<sup>d</sup> Deactivated sample after two regeneration cycles in  $O_2$ .

<sup>e</sup> Based on total uptake.

## RESULTS

The results from hydrogen chemisorption at 300 K on fresh Pd and Pt catalysts are given in Table 1. Dispersions for Pd ranged from 0.18 to 0.49. The  $H_{rev}/Pd_b$  values, where  $H_{rev}$  is the reversible H adsorption and  $Pd_b$  is the number of bulk Pd atoms, i.e.,  $Pd_{total}-Pd_s$ , generally fell between 0.4 and 0.7. The high  $H_{rev}/Pd_b$  value of 1.1 for the most highly dispersed sample can be attributed to a large contribution from reversible chemisorption in addition to bulk

hydride formation (14). The low values for the calcined 0.59% Pd/ $SiO_2$ - $Al_2O_3$  samples may indicate incomplete reduction of the Pd. The hydrogen uptakes on used and regenerated samples are reported in Table 2. Significant loss of accessible Pd surface area occurred during the reaction and the irreversible uptakes were significantly lower than those on fresh samples. The deactivated catalysts were regenerated in a flowing mixture of 20%  $O_2$ /80% He at 673 K for 1 h. The irreversible uptake on 1.67% Pd/ $\eta$ - $Al_2O_3$  increased but was not restored to the original value for the fresh sample. Another oxygen treatment did not change the irreversible uptakes on this catalyst. A sample of 1.64% Pd/ $SiO_2$ - $Al_2O_3$  used only for chemisorption was also subjected to an oxygen regeneration treatment after which it was reduced at 448 K. The irreversible and reversible uptakes, as well as the apparent hydride ratios, were lower compared to the fresh reduced sample, which implied that some sintering had occurred. The irreversible uptakes on the deactivated samples which were not cleaned by calcination and only treated in  $H_2$  were strikingly lower than uptakes on the fresh sample, but they increased after a calcination treatment. This strongly suggests that a carbonaceous deposit existed on the Pd surface after the reaction was completed which could be oxidized off. The particle diameters calculated for the two contaminated samples consequently do not represent particle size accurately. Regardless, some sintering appeared to have occurred during time on stream and the subsequent pretreatments. The oxygen treatment could have altered the size distribution of particles in the catalyst, thereby reducing the number of extremely small particles and hence the amount of reversibly chemisorbed hydrogen, which would also explain the lower  $H_{rev}/Pd_b$  ratios.

Table 3 lists the benzene turnover frequencies, TOF<sub>b</sub>, obtained with these catalysts at a standard set of reaction conditions along with one TOF for toluene. These represent values with only one component in the feed. The 1.67%

TABLE 3

Hydrogenation of Pure Benzene (or Toluene) on Pd and Pt Catalysts at 353 K

Catalyst	$T_r^a$ (K)	Irreversible		TOF <sub>B</sub> <sup>b</sup> ( $s^{-1} \times 10^3$ )
		$H_2$ uptake ( $\mu$ mole/g)	Rate <sub>benzene</sub> ( $\mu$ mole/g-s)	
1.67% Pd/ $\eta$ - $Al_2O_3$	673	32.5	0.37	5.7
1.67% Pd/ $\eta$ - $Al_2O_3$	673	3.8	0.02	3.0 <sup>e</sup>
0.22% Pd/ $SiO_2$ - $Al_2O_3$	448	5.0	0.23	23.0
0.59% Pd/ $SiO_2$ - $Al_2O_3$	573 <sup>d</sup>	7.3	0.40	27.6
0.59% Pd/ $SiO_2$ - $Al_2O_3$	573	7.8	0.42	27.3
0.59% Pd/ $SiO_2$ - $Al_2O_3$	448	5.0	0.18	17.6
1.64% Pd/ $SiO_2$ - $Al_2O_3$	448	37.5	2.3	31.0
1.64% Pd/ $SiO_2$ - $Al_2O_3$	448	21.3	0.64	15.0 <sup>e</sup> (11.5) <sup>e</sup>
1.64% Pd/ $SiO_2$ - $Al_2O_3$	673	20	0.13	3.2
1.64% Pd/ $SiO_2$ - $Al_2O_3$	673	6.5	0.04	3.2 <sup>e</sup>
3.61% Pd/C	573	30	0.49	8.1
0.78% Pt/ $\eta$ - $Al_2O_3$	723	22.0 <sup>f</sup>	3.0	75

Note.  $P_{H_2} = 680$  Torr;  $P_{aromatic} = 50$  Torr.

<sup>a</sup> Pretreatment A, reduction temperature.

<sup>b</sup> Based on steady-state activity and uptake on fresh sample.

<sup>c</sup> Deactivated sample, based on final activity and uptake on used sample.

<sup>d</sup> Pretreatment B, calcined.

<sup>e</sup> For toluene.

<sup>f</sup> Total uptake.

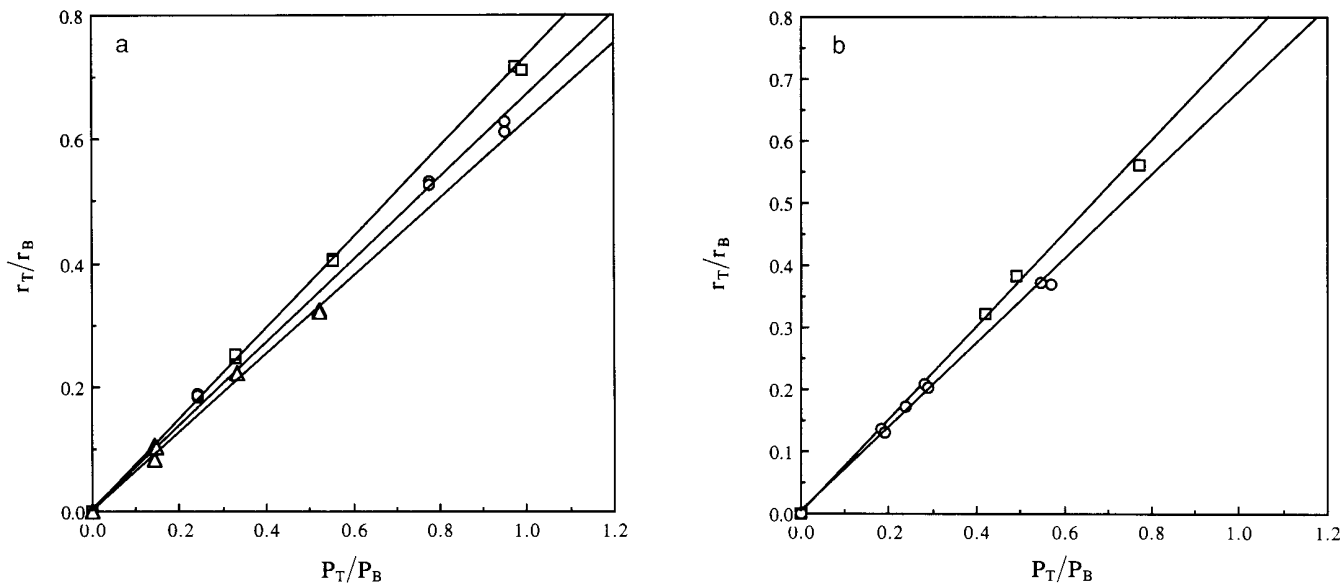


FIG. 1. Relative rate of toluene and benzene hydrogenation ( $r_T/r_B$ ) vs. ratio of partial pressures. ( $P_T/P_B$ ) (a) at 353 K: (○) 0.22% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; (□) 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; (△) 1.67% Pd/Al<sub>2</sub>O<sub>3</sub>. (b) Over 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ( $T_r = 448$  K) at (□) 313 K; (○) 353 K.

Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst yielded a TOF in excellent agreement with prior values (ca.  $5.0 \times 10^{-3} \text{ s}^{-1}$ ) obtained in this laboratory (2). The TOFs for 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> are significantly higher after reduction at 448 K than after reduction at 673 K, in accordance with previous results, and these TOF values compare well with that for 0.22% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> after reduction at 448 K and also with that for 0.59% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> after reduction at 573 K. The TOFs for 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ( $T_r = 673$  K) were about one-fourth the value reported previously, but significant *in situ* deactivation due to pinhole air leaks initially present in the reactor appeared to be responsible for this observation. The TOF of  $75 \times 10^{-3} \text{ s}^{-1}$  for Pt/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> is near the average value of  $64 \times 10^{-3} \text{ s}^{-1}$  reported by Lin and Vannice (4), and it is higher than the corresponding values for Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> by a factor of 15.

The relative rate of toluene and benzene hydrogenation with an equimolar gas mixture,  $R_{T/B}$ , is obtained from a plot of the relative rate,  $r_T/r_B$ , vs  $P_T/P_B$  (9), such as those in Figs. 1a–1b. The  $R_{T/B}$  values for the Pd catalysts which are listed in Table 4 do not vary much and range from 0.58 to 0.73. These values of less than one indicate that toluene is less reactive than benzene on Pd catalysts, whereas the threefold higher  $R_{T/B}$  value for Pt indicates that toluene hydrogenation is favored on Pt. When combined with plots of  $r_B^0/r_B$  versus  $P_T/P_B$ , where  $r_B^0$  is the rate of hydrogenation of benzene with a pure benzene feed, both  $K_{T/B}$  values, i.e., the ratio of adsorption equilibrium constants for toluene and benzene, and the ratio of apparent rate constants,  $k_{T/B}$  can be obtained. These values, from plots such as those in Figs. 2a–2b are also tabulated in Table 4. A  $K_{T/B}$  value close to unity is typically interpreted to mean that benzene and

toluene are nonselectively adsorbed, while higher values have been assumed to imply that toluene is preferentially adsorbed. The effect of both reduction temperature and reaction temperature on  $R_{T/B}$  and the kinetic parameters obtained during competitive hydrogenation were investigated for 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 0.22% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 1.67% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, and 0.78% Pt/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, and the results are reported in Table 5. In general, the  $R_{T/B}$  values were not strongly affected by variations in either temperature over

TABLE 4  
Kinetic Parameters for Pd and Pt Catalysts at 353 K

Catalyst	$T_r^a$ (K)	$K_{T/B}$	$k_{T/B}$	$R_{T/B}$	TOF <sub>B+T</sub> <sup>b</sup> (s <sup>-1</sup> × 10 <sup>3</sup> )
1.67% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	673	0.9	0.70	0.63	4.9
1.67% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	673	0.9	0.74	0.64	2.6
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.6	0.46	0.73	20.6
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	448	1.8	0.38	0.68	9.0
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	673	1.0	0.58	0.58	2.5
0.22% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.6	0.43	0.67	14.8
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.5	0.39	0.58	11.1
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	573	2.0	0.38	0.75	15.9
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	448	2.0	0.31	0.61	30.0
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	573	1.8	0.39	0.68	16.6
3.61% Pd/C	573	1.3	0.47	0.63	5.7 <sup>e</sup>
0.78% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	723	3.8	0.47	1.8	39.8

Note.  $P_{H_2} = 680$  Torr;  $P_{aromatic} = 50$  Torr.

<sup>a</sup> Pretreatment A, reduction  $T$ .

<sup>b</sup> Equimolar feed mixture.

<sup>c</sup> Deactivated sample.

<sup>d</sup> Pretreatment B, calcined.

<sup>e</sup>  $P_{Arom} = 12$  Torr.

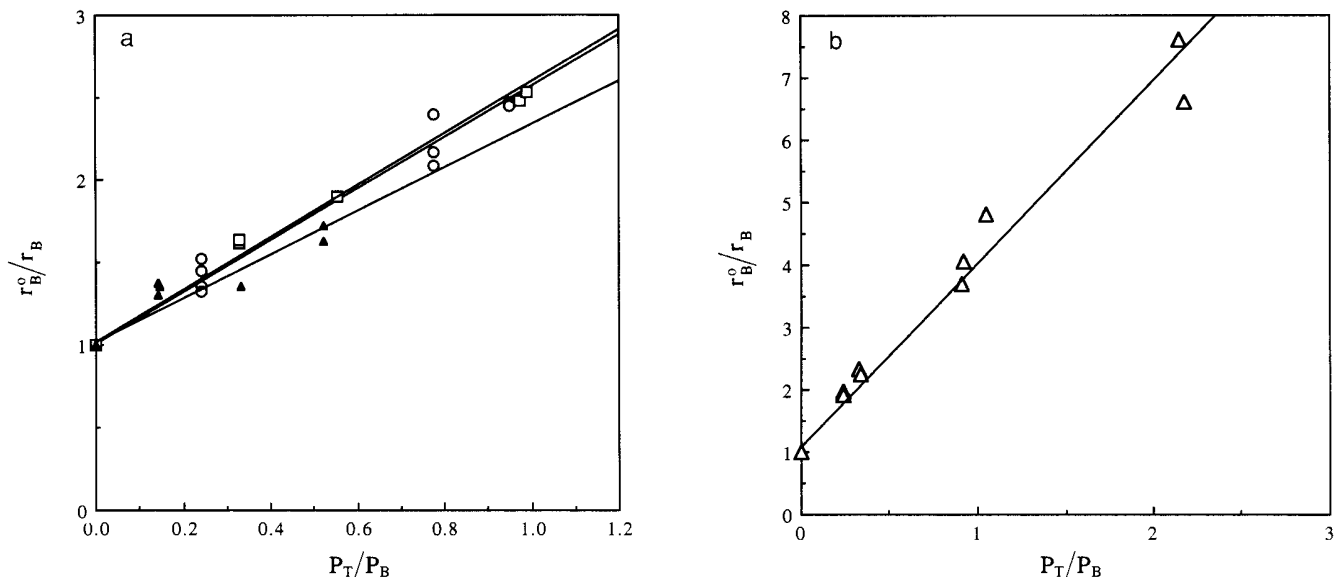


FIG. 2. Relative benzene hydrogenation rate vs ratio of partial pressures at 353 K: (a) (○) 0.22% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; (□) 1.64% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; (△) 1.67% Pd/Al<sub>2</sub>O<sub>3</sub>. (b) 0.78% Pt/Al<sub>2</sub>O<sub>3</sub>.

the range employed; however,  $K_{T/B}$  values increased, while  $k_{T/B}$  values decreased with increasing temperature. By subtracting the contribution of the Pd to the overall rate (12), the kinetic parameters associated with the acid sites on the oxide support were calculated for an equimolar mixture of benzene and toluene for Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts and the values, designated by an I, are listed in Table 6. The  $R_{T/B}^I$  and  $k_{T/B}^I$  values varied from 0.53 to 0.77 and 0.27 to 0.48, respectively, and the  $K_{T/B}^I$  values for the oxide sites were higher than those for Pd.

## DISCUSSION

The impetus behind this study was to determine if relative reaction rates during the hydrogenation of aromatic

hydrocarbon mixtures over Pd or Pt could be altered by the use of an acidic support such as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and, if so, to better understand why. For example, compared to Pd dispersed on a nonacidic support, benzene hydrogenation over Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> could be enhanced by a factor of 20 or more, whereas toluene hydrogenation increased by a factor of only 6 to 8 (3). Thus the possibility existed that benzene hydrogenation over Pd from a benzene/toluene mixture could be selectively facilitated by the use of an acidic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support. The capability to selectively hydrogenate certain aromatics from a mixture could have useful applications.

In agreement with earlier studies (2, 3), the Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts in this study again verified that higher turnover frequencies are obtained after mild reduction compared to values obtained either after reduction at 673 K or with Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> and Pd/C catalysts, as shown in Table 3.

TABLE 5

Influence of Reduction and Reaction Temperatures on Kinetic Parameters

Catalyst	$T_r$ (K)	$T_{rxn}$ (K)	$K_{T/B}$	$k_{T/B}$	$R_{T/B}$	TOF <sub>B+T</sub> (s <sup>-1</sup> × 10 <sup>3</sup> )
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	673	353	1.0	0.58	0.58	2.5
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	673	363	1.1	0.56	0.61	3.1
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	353	1.8	0.38	0.68	20.6
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	313	1.4	0.53	0.75	1.7
0.22% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	353	1.6	0.43	0.67	14.8
0.22% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	333	1.3	0.46	0.60	5.4
1.67% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	673	353	0.9	0.70	0.63	4.9
1.67% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	673	373	1.2	0.55	0.66	11.6
0.78% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	723	313	3.0	0.54	1.6	6.7
0.78% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	723	353	3.8	0.47	1.8	39.8

Note.  $P_B + P_T = 50$  Torr.

TABLE 6

Kinetic Parameters for Acid Sites on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

Catalyst	$T_r$ (K)	$K_{T/B}^I$	$k_{T/B}^I$	$R_{T/B}^I$	TOF <sub>B+T</sub> (s <sup>-1</sup> × 10 <sup>3</sup> )
0.22% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.9	0.35	0.67	10.0
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.8	0.42	0.77	15.7
1.64% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	673	1.1	0.48	0.53	1.32
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	573	2.2	0.33	0.71	11.8
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	448	1.9	0.28	0.53	6.6
0.59% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	573	2.5	0.27	0.68	10.3

Note.  $T_{rxn} = 353$  K;  $P_T = P_B = 25$  Torr.

<sup>a</sup> Pretreatment B, calcined.

However, as demonstrated by the relative hydrogenation rates for toluene and benzene listed in Tables 4 and 5, the  $R_{T/B}$  values for the most acidic Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts, i.e., those reduced at 448 K which leaves chloride on the surface, are not markedly different from those for the Pd/C and Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalysts. In fact, the  $R_{T/B}$  values tend to be higher than those for the latter catalysts, whereas they were anticipated to be lower should the relative hydrogenation rates of the single-component feeds be maintained in the mixture. Thus some form of compensation occurs which results in similar concurrent hydrogenation rates regardless of the support utilized.

One explanation for significant variations in turnover frequencies for aromatic hydrocarbon hydrogenation has been that the metal particles were electron deficient, thereby altering the metal-adsorbate bond strength (1, 9, 15-17). This would seem to have applicability to very small particles, such as metal clusters in a zeolite; however, this rationale is much more difficult to apply to the much larger metal crystallites present on these oxide supports. An alternate explanation for the higher activity when acidic supports are utilized is that acidic sites on the support can adsorb aromatic hydrocarbons and, if these sites are supplied by spilled-over hydrogen, they can also contribute to the overall activity (6-8). To examine these two possibilities in greater detail, the general approach of Massardier and co-workers was utilized (9, 15-17), i.e., both the relative rate of toluene and benzene hydrogenation,  $r_T/r_B$ , and that for hydrogenation of benzene only versus that in the mixture,  $r_B^0/r_B$ , were determined as a function of the ratio of the two partial pressures,  $P_T/P_B$ . This allows the determination of not only the ratio of adsorption equilibrium constants,  $K_{T/B}$ , which have been used by Massardier *et al.* to probe the relative bond strength of benzene and toluene, but also the ratio of rate constants,  $k_{T/B}$ , which have not been previously discussed. A detailed mechanism was not given to explain the Langmuir-Hinshelwood (L-H) rate expression used to describe the hydrogenation of benzene (B) and toluene (T) mixtures, i.e.,

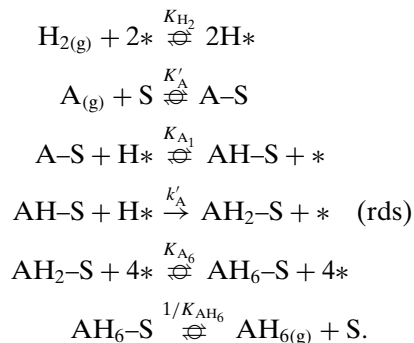
$$r_B = f_{H_2} k_B K_B P_B / (1 + K_B P_B + K_T P_T) \quad [1]$$

and

$$r_T = f_{H_2} k_T K_T P_T / (1 + K_B P_B + K_T P_T) \quad [2]$$

in which the functionality on H<sub>2</sub> pressure,  $f_{H_2}$ , was not specified and it was assumed to remain constant and identical for both reactions (9). However, the only reaction models which give such an expression, i.e., the denominator is not squared, are either one assuming aromatic adsorption is the rate determining step (rds) or one proposing that a second type of site exists for hydrogen adsorption and H addition to the adsorbed aromatic is the rds. The former possibility is very unlikely, whereas the latter has been routinely assumed in previous studies (6-8 and references

therein). Furthermore, on Pt and Pd the H<sub>2</sub> pressure dependencies typically fall between 1/2 and 1 thus strongly implying that addition of the second H atom (or reaction with an adsorbed, activated H<sub>2</sub> molecule) is the rds if routine L-H assumptions are made (6-8); i.e., the catalytic sequence would be



Here \* and S represent sites for hydrogen and the aromatic hydrocarbon (A), respectively, and AH<sub>6</sub> is the cyclic paraffin. The derived rate expressions for benzene or toluene in a mixture are those shown previously by Eqs. [1] and [2]. With the previous assumptions one can readily show that

$$r_T/r_B = (k'_T K_{T_1} K'_T / k'_B K_{B_1} K'_B) (P_T/P_B), \quad [3]$$

thus

$$R_{T/B} = (k_T/k_B) (K'_T/K'_B) = k_{T/B} K_{T/B}, \quad \text{where } k_A = k'_A K_{A_1} \quad [4]$$

from the previous reaction sequence, and

$$r_B^0/r_B = 1 + K_{T/B} (P_T/P_B). \quad [5]$$

Thus both  $k_{T/B}$  and  $K_{T/B}$  can be obtained; however,  $k_{T/B}$  contains a ratio of four constants, not two, an aspect not clarified previously. An identical mathematical form of the rate expression, which contains an additional constant to represent hydrogen spillover, can be derived for sites on the support surface (7, 8, 12).

The  $K_{T/B}$  values for Pd/Al<sub>2</sub>O<sub>3</sub> in Table 4 are near unity, in agreement with the value for Pd/SiO<sub>2</sub> reported by Phoung *et al.* (16) and that estimated from single reactant values (7), while a value of 2.0 for Pd/SiO<sub>2</sub> was reported by Larsen and Haller (18). A comparison of the  $k_{T/B}$  values implies that a molecule of toluene hydrogenates more slowly than a benzene molecule, and a clear trend exists such that lower  $k_{T/B}$  values correlate with higher  $K_{T/B}$  values. Consequently, this compensation results in relative rates that do not vary markedly, as indicated by the  $R_{T/B}$  values. The  $K_{T/B}$  values for the Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are higher, consistent with previous results with acidic supports, and with this model they imply that toluene is more strongly bound than benzene on these catalysts, according to the argument of Massardier *et al.* (9). However,  $K_{T/B}$  values at different temperatures were obtained in the present study for Pd/Al<sub>2</sub>O<sub>3</sub>,

Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub>, as shown in Table 5; consequently, a plot of  $\ln K_{T/B}$  vs.  $1/T$  gives the difference in heats of adsorption ( $Q_T - Q_B$ ). A zero-order dependence on benzene exists over this entire temperature range (2, 6). In all cases, these differences were negative, i.e., -3.8, -2.4, and -1.3 kcal/mole, respectively (12), thus indicating that benzene is more strongly bound than toluene despite evidence to the contrary for Group VIII metals (19-22). The heat of adsorption of benzene on Pd(111) has been determined from TPD experiments to be 24 kcal/mole (23), which is close to  $Q_{ad}$  values for Ni, Rh, and Pt (24-26). This internal inconsistency is another reason we believe that the electron-deficient model may not be appropriate for these larger crystallites. However, if the acid site model is chosen and rates on the interfacial acid sites alone are calculated, a plot of  $K_{T/B}^I$  vs  $1/T$  for Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> again gives a negative  $Q_T - Q_B$  value (12). Since literature information indicates that toluene is also expected to be more strongly adsorbed than benzene or oxide supports (27-31), this inconsistency is still not resolved. As a result of this analysis, the previous model and interpretation used by Massardier and co-workers may be too simplistic and must be considered suspect.

The model described previously assumed that adsorbed benzene and toluene were the only significant surface species and the presence of any hydrogen-deficient aromatic compounds was not considered; however, there is ample evidence that such species are indeed formed, as discussed elsewhere (7, 8, 12). For example, evidence from TPD studies of benzene on Pd (32-34), benzene chemisorption (35, 36), magnetic susceptibility measurements (37, 38), and isotopic exchange reactions (39) indicates that dehydrogenation can also occur. Phenyl groups have been identified on metal surfaces (40-42), and they have also been proposed as intermediates in the H<sub>2</sub>/D<sub>2</sub> exchange reaction (43). A tilted adsorbed configuration for benzene on Pd (111) has implied that existence of  $\sigma$ -bonded species (44), i.e., a H-deficient species consistent with phenyl groups. Consequently, a model including this possibility appears to be more descriptive of the actual surface and it was therefore adopted. It is the same as the prior sequence of steps except that quasiequilibrated, H-deficient surface species are allowed to exist, and the addition of the first H atom is assumed to be the rds. This model has been described in detail elsewhere (8, 12). Along with this shift in the rds, if the aromatic reactant is assumed to be present at low fractional surface coverages and a single H-deficient species (such as phenyl or tolyl) is assumed to predominate on the surface, the derived rate expression simplifies to the form

$$r = \frac{k'_A K_{H_2}^{1/2} K'_A P_{H_2}^{1/2} P_A}{(1 + K_{H_2}^{1/2} P_{H_2}^{1/2})(1 + K'_A K_{A_i}^D K_{H_2}^{-i/2} P_A P_{H_2}^{-i/2})}, \quad [6]$$

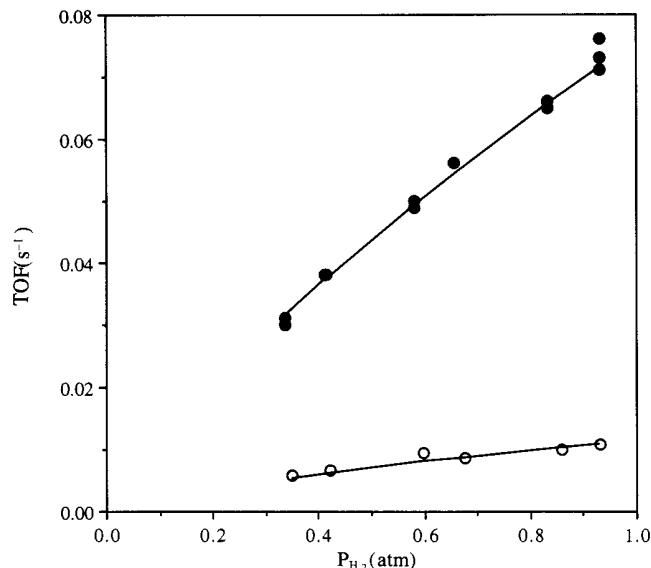


FIG. 3. Specific activity vs H<sub>2</sub> partial pressure for benzene hydrogenation over 1.67% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, from model invoking H-deficient surface species with  $i = 1$  (benzyl): (●)  $T_{rxn} = 413$  K; (○)  $T_{rxn} = 373$  K.

where  $K_{A_i}^D$  is the equilibrium constant for the formation of the dominant H-deficient species which has lost  $i$  hydrogen atoms (8, 12).

This equation with three adjustable parameters was fit to the data for the hydrogenation of benzene alone at three different temperatures using a Gauss-Newton nonlinear regression method with a convergence criterion of  $10^{-8}$  (12). Optimum results were obtained with  $i = 1$  and the fits were quite satisfactory, as shown in Figs. 3 and 4. A similar ap-

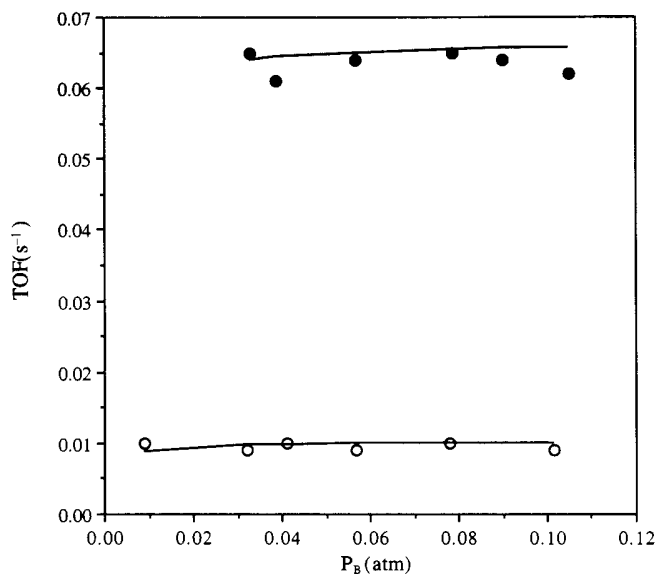


FIG. 4. Specific activity vs Bz partial pressure for benzene hydrogenation over 1.67% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, from model invoking H-deficient surface species with  $i = 1$  (benzyl): (●)  $T_{rxn} = 413$  K; (○)  $T_{rxn} = 373$  K.

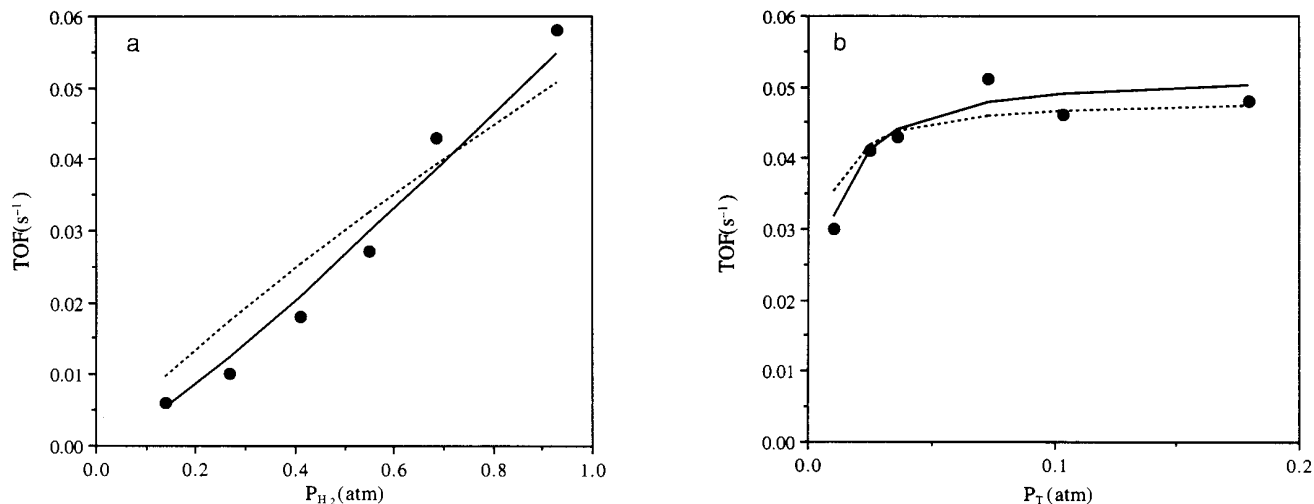


FIG. 5. Specific activity vs reactant partial pressure for toluene hydrogenation over 1.67% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> at 413 K, from model invoking H-deficient surface species.  $i = 1$ , dotted line;  $i = 2$ , solid line; (a) for H<sub>2</sub>; (b) for toluene.

proach with the toluene data indicated that the best fits were obtained with  $i = 2$ , but satisfactory fits were also attained with  $i = 1$ , as shown in Fig. 5. If  $i = 1$  is chosen as an acceptable value for toluene so that the form of the two-rate equations is identical and the general approach of Massardier (9) can again be used, then it can be shown in this case (12) that

$$r_B^0/r_B = 1 + (K'_T/K'_B)(K_T^D/K_B^D)(P_T/P_B), \quad [7]$$

$$r_T/r_B = (k'_T/k'_B)(K'_T/K'_B)(P_T/P_B), \quad [8]$$

$$k_{T/B} = (k'_T/k'_B)(K_B^D/K_T^D), \quad [9]$$

and

$$K_{T/B} = (K'_T/K'_B)(K_T^D/K_B^D), \quad [10]$$

and the relative coverage of the H-deficient species is

$$\theta_{T_1}/\theta_{B_1} = K_{T/B}(P_T/P_B). \quad [11]$$

In other words the *apparent*  $K_{T/B}$  term is now the ratio of two sets of parameters, rather than just the equilibrium adsorption coefficients. This can resolve the apparent contradiction discussed earlier regarding relative adsorption strengths. Furthermore, Eq. [10] shows that the  $K_{T/B}$  value can reflect the influence of dehydrogenated species as well as the adsorption bond strength; thus a simple interpretation of  $K_{T/B}$  values may not be warranted. Abon *et al.* found that toluene dehydrogenates to a greater extent than benzene on Pt(111), as over 95% of the adsorbed toluene dehydrogenated during TPD (20), while Muertterties and co-workers verified that toluene dissociates more easily than benzene on Pt and also showed that aromatic molecules on Pd dehydrogenated during TPD (25, 45). Deuterium

exchange reactions of alkylbenzenes on metals have indicated that the H atoms in alkyl groups exchange more rapidly than H atoms in ring positions (46, 47). The higher  $K_{T/B}$  values for Pt compared to those for Pd may represent a greater extent of toluene dissociation on the active surface, compared to benzene, as well as a difference in initial bond energy. Finally, it should be emphasized that if the H-deficient surface species formed differ in the number of H atoms lost, i.e.,  $i_B \neq i_T$ , then the H<sub>2</sub> functionality does not cancel out and it also multiplies  $K'_T/K'_B$  in Eq. [7] (12). The approach of Massardier *et al.* is then inapplicable. The possibility that this may occur and  $i_B = 1$  whereas  $i_T = 2$  is not inconsistent with data that indicate toluene dehydrogenates to a greater extent than benzene on metals and oxides (20, 28). As mentioned, this introduces an additional term,  $1/K_{H_2}^{1/2} P_{H_2}^{1/2}$ , in Eq. [7] and invalidates any simple interpretation of the apparent  $K_{T/B}$  term.

As with the first sequence of steps, this latter model can be easily altered to include a contribution from acid sites on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> surface, i.e., it contains only an additional step for hydrogen spillover (8, 12). Therefore,  $K_{T/B}^I$  and  $k_{T/B}^I$  values can again be calculated for these sites on the support, and they are listed in Table 6. The  $K_{T/B}^I$  values are higher than those for the Pd surface, while the  $k_{T/B}^I$  values are lower; thus, the relative rates on these sites,  $R_{T/B}^I$ , are little different from those for Pd/Al<sub>2</sub>O<sub>3</sub>. Kamball and co-workers found that deuterium exchanged with hydrogen in the ring positions of benzene, toluene, and *m*-xylene at the same rate over Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> with no directing effect due to the methyl groups (46-48). During TPD from SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, 5-8% of the toluene dehydrogenated, while 1-2% of the benzene dehydrogenated (28). As mentioned earlier, toluene is more strongly bound than benzene on acidic oxides (27-31). The higher  $K_{T/B}^I$  values



obtained for these oxide sites are consistent with these results and this behavior could also account for the higher values observed with acidic zeolite supports. The presence of more strongly bound, H-deficient toluene species in benzene/toluene mixtures would inhibit the rate of both reactions, but with a greater influence on benzene—this may be the reason for the absence of a selective enhancement of benzene hydrogenation over Pd in these mixtures.

The extrapolated  $K_{T/B}$  value at 298 K of 2.7 for Pt/ $\eta$ - $Al_2O_3$  compares to that 4.0 for Pt sponge but is substantially lower than the value for 8.0 for Pt/SiO<sub>2</sub> (9, 16). Massardier and co-workers reported respective  $K_{T/B}$  values of 7, 8, and 13 for Pt(111), Pt(100), and Pt(110) single-crystal surfaces (49); consequently, the lower  $K_{T/B}$  values are not explained by simple surface geometry arguments. Again, variations in the formation of H-deficient surface species brought about by different reaction conditions could account for these variations. The addition of Sn(50) and Bi(51) to Pt surfaces has been shown to suppress or eliminate benzene dehydrogenation and this behavior was associated with an ensemble size effect; however, the role of Sn appeared to be more than just a simple site blocker. This again implies that the apparent  $K_{T/B}$  parameters derived from these kinetic analyses can depend on more than one variable and they must be interpreted with caution.

### SUMMARY

Mixtures of benzene and toluene produced rates of hydrogenation over Pd that were relatively invariant to the support, the reduction temperature, and the reaction temperature. A simple two-site model that has been used in the past to evaluate apparent ratios of adsorption constants was applied to the results obtained here, and some internal inconsistencies related to the temperature dependence of these ratios were noted. An alternative model assuming the formation of hydrogen-deficient surface species under reaction conditions is supported by other studies in the literature, and it is able to resolve the apparent discrepancy. However, the interpretation that these apparent  $K_{T/B}$  ratios represent only relative bond strengths is not appropriate, and analysis of the kinetic model shows that they can also reflect the relative formation of H-deficient species like phenyl or tolyl groups. As a result, the variations in these  $K_{T/B}$  values must be interpreted with caution because they very likely indicate the propensity of the metal to form rate-inhibiting surface species rather than differences in the electron deficiency of metal particles. Consequently, with this perspective the wide range of reported  $K_{T/B}$  values can be better understood.

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