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The Hydrogenation of Toluene and *o*-, *m*-, and *p*-Xylene over Palladium

I. Kinetic Behavior and *o*-Xylene Isomerization

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The vapor-phase hydrogenation of toluene and *o*-, *m*-, *p*-xylene was studied over Pd powder and Pd dispersed on MgO, SiO_2, Al_2O_3, SiO_2–Al_2O_3, and TiO_2. As with benzene, the use of the last two acidic oxides can markedly enhance activities, but the relative change diminishes as methyl groups are added; for example, the average enhancement in turnover frequency was 8 for toluene while the lowest was 3 for *m*-xylene. The turnover frequency decreased in the following order: benzene > toluene ≥ *p*-xylene ≥ *m*-xylene > *o*-xylene; however, the differences were less pronounced for Pd powder and Pd/MgO compared to Pd/SiO_2–Al_2O_3 and Pd/TiO_2. This trend is attributed to an electronic effect on the aromatic ring related to the addition of methyl groups although steric hindrance also appears to be responsible for the consistently low rates for *o*-xylene hydrogenation. All reactions were first order in H_2 and zero order in the aromatic compound, and activation energies were near that of benzene and did not vary significantly, as average values were 11.8, 12.0, 12.7, and 13.7 for toluene, *m*-xylene, *o*-xylene, and *p*-xylene, respectively. Isomerization of *o*-xylene to *m*-xylene was observed over all the Pd catalysts, but rates were fivefold higher on the most acidic Pd/SiO_2–Al_2O_3 and Pd/TiO_2 catalysts thus verifying the presence of acid sites on the support.

INTRODUCTION

The hydrogenation of aromatic hydrocarbons is of interest not only because of the commercial use of this reaction (*1*), but also because the upgrading of coal liquids involves the hydrogenation of aromatic rings. Thus, studies of model aromatic compounds may provide improvements in these processes. Benzene hydrogenation is considered a structure-insensitive reaction (*2–5*), and numerous studies have been conducted on the adsorption and reaction of this molecule. However, fewer studies on toluene and the three xylene isomers have been conducted and no steady-state specific activities are available in the literature. In addition to this situation, significant support effects have been found for benzene hydrogenation over Pd, and the use of acidic oxides can markedly enhance specific activities (*6–9*). It is therefore of interest to determine if similar behavior continues as methyl groups are added to the benzene ring and to determine if electronic and steric effects due to these groups can be observed.

A detailed reaction sequence has been proposed for benzene which invokes additional acidic adsorption sites in the metal-support interfacial region for the aromatic compound along with its reaction with hydrogen migrating from the Pd surface (*9*). A comparison of the kinetic behavior of toluene and *ortho-*, *meta-*, and *para*-xylene with that of benzene would test this model and also provide insight about the similarity of the surface chemistry involved. A particularly useful probe is provided by the parallel isomerization reaction of *o*-xylene to *m*-xylene, which occurs on acid sites via a carbonium ion mechanism as well as on the Pd surface itself. We have used a well-charac-

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terized family of Pd catalysts, some of which were employed in our previous study on benzene hydrogenation. The kinetic behavior for hydrogenation is discussed in this paper, while the reaction model and isomerization results are presented in the following article (*10*).

EXPERIMENTAL

Catalyst Preparation and Pretreatment

The support materials used were SiO_2 (Davison Grade 57, 220 m^2/g), *n*-Al_2O_3 (Exxon Research and Engineering Co., 245 m^2/g), TiO_2 (Degussa P25, 80% anatase, 20% rutile, 50 m^2/g), SiO_2–Al_2O_3 (Davison Grade 979, 400 m^2/g), and MgO (Alfa Products, 45 m^2/g). Prior to their use all supports were calcined in flowing air at 773 K for 2 h. Pure Pd powder (Puratronic Grade, 99.999%), was obtained from Johnson Matthey Chemicals.

The 1.1% Pd/TiO_2, 1.1% Pd/SiO_2–Al_2O_3, and 0.54% Pd/Al_2O_3 catalysts were made by an incipient wetness technique using $PdCl_2$ (Aldrich Chemicals), dissolving it in HCl and evaporating to near dryness twice, adding distilled deionized water to obtain the required volume, and then adding this solution dropwise to the calcined support using thorough stirring after each drop (*11*). The catalysts were dried overnight in air at 393 K, bottled, and stored in a desiccator. The HCl-impregnated TiO_2 and SiO_2–Al_2O_3 samples were made by adding as much chlorine as that contained in the Pd/TiO_2 and Pd/SiO_2–Al_2O_3 samples. The Pd/SiO_2 catalyst was prepared from $Pd(NH_3)_4(NO_3)_2 \cdot 2H_2O$ (Spex) using an ion-exchange technique (*12*). The Pd/MgO was prepared by an incipient wetness technique using palladium acetylacetonate (Aldrich Co.) dissolved in benzene (Baker Analyzed) along with several impregnation steps because of the low solubility of $Pd(acac)_2$ in benzene (*13*). This catalyst was dried in air at 300 K overnight before storage in the desiccator.

The Pd weight loadings were measured on the air-dried samples by plasma emission spectroscopy at the Mineral Constitution Laboratory on campus, and all values were within 10% of nominal loadings.

Each fresh catalyst sample was pretreated by flowing 50 cc min^{-1} of helium at 0.1 MPa at 300 K for 30 min then at 393 K for 1 h. The flow was then switched to 50 cc min^{-1} of hydrogen at 0.1 MPa and the sample was reduced at either 393 or 448 K for 1 h. When the final reduction temperature was 673 K the He was flowed at 393 K for 30 min and at 533 K for 30 min prior to the 1-h reduction. Each pretreatment is identified in the tables by the reduction temperature, T_r.

All catalysts were characterized by hydrogen chemisorption in a volumetric adsorption system capable of a vacuum below 10^{-6} Torr (*11*). The dual isotherm technique of Boudart and co-workers was utilized (*14, 15*), which also allows an estimate of bulk hydride phase formation, except for the Pd powder where Aben's method was used (*16*). Adsorption on the used samples after the kinetic studies was the same as, or slightly less than, the fresh samples (*17*). Since the amounts of used samples were about one-tenth that of the fresh samples, thus introducing greater uncertainty, only uptakes on fresh catalysts are given here. The isotherms were extrapolated to zero pressure to correct for adsorption on the support and to determine both the irreversible and reversible hydrogen adsorption, H_{ad} and H_{rev}, respectively, at 300 K.

Kinetic Measurements

Benzene (Baker Analyzed) was obtained from the J. T. Baker Co., toluene (HPLC Grade, 99.9+%) and *o*-xylene (anhydrous, 97+%) from the Aldrich Co., and *m*-xylene (99.8%) and *p*-xylene (99.8%) from the Kodak Chemical Co. Hydrogen (99.999%) and helium (99.999%) (Linde Specialty Gases) were further purified by flowing them through Oxy-traps (Alltech Associates).

Typically, 0.1–0.2 g catalyst was loaded into the glass reactor and the chosen pretreatment was employed after which the reactor was cooled to about 373 K. Using a Sage pump the liquid hydrocarbon feed was introduced through a stainless steel (SS) capillary tube into a heated 0.25″ SS line maintained at a temperature far above the boiling point of the hydrocarbon. The hydrocarbon vapor mixed with the H_2 (or H_2 + He) carrier gas, which was controlled by micrometer valves and measured by Hastings–Raydist mass flowmeters, then passed through the catalyst bed. The temperature of the catalyst bed was maintained in a temperature-controlled, fluidized sandbath (Techne Inc.) and monitored by a thermocouple at the bed exit. The exit gas stream was analyzed with a gas chromatograph (Hewlett–Packard, Model 700-00) fitted with a thermal conductivity detector, an electronic integrator (Perkin–Elmer, LCI-100), and 6-ft, ⅛-in-ID SS columns packed with Carbowax 20M. An isothermal temperature of 340 K was maintained.

Most experiments were conducted over a temperature range of 373–423 K. The reactor was operated at atmospheric pressure, which was typically near 730 Torr, and standard conditions were pressures of 680 Torr for H_2 and 50 Torr for the aromatic hydrocarbon. Conversions were kept below 15% to avoid heat and mass transfer effects. Values of the Weisz criterion were below 5×10^{-5}, which clearly showed that the results were free from diffusional limitations (*18*). A bracketing technique was employed in the kinetic runs (*7*), and five data points were usually obtained while the temperature was increased and two data points were taken as the temperature was decreased to check for any deactivation.

Reaction orders were determined with respect to H_2 and the aromatic hydrocarbon for the hydrogenation of toluene, *o*-xylene,and *m*-xylene over the Pd/Al_2O_3 and $Pd/SiO_2–Al_2O_3$ catalysts. Using He as a makeup gas, the partial pressure of hydrogen was varied from 680 to 100 Torr at a constant hydrocarbon pressure of 50 Torr, and the hydrocarbon partial pressure was varied between 70 and 5 Torr at a constant H_2 pressure of 600 Torr. In both cases, five data points were obtained with decreasing partial pressure and two with increasing pressure. For toluene, pressure dependencies were determined at 363 K for $Pd/SiO_2–Al_2O_3$ and at 413 K for Pd/Al_2O_3, whereas for *m*-xylene and *o*-xylene, 413 K was used for $Pd/SiO_2–Al_2O_3$ and 438 K for Pd/Al_2O_3 because of the lower activity of the latter. The behavior of *p*-xylene has been reported to be very similar to that of toluene (*19*); hence the reaction orders of *p*-xylene hydrogenation were not determined.

RESULTS

H_2 *Chemisorption*

The results of the hydrogen uptake studies on fresh reduced catalyst samples are in Table 1. The Pd dispersion, *D*, defined as the ratio of Pd surface atoms, Pd_s, to the total number of the Pd atoms, Pd_t, was determined for each catalyst assuming $H_{ad}/Pd_s = 1$. The apparent bulk β-hydride phase composition is represented as H_{rev}/Pd_b, assuming that $H_{ab} = H_{rev}$ and $Pd_b = Pd_t - Pd_s$. The irreversible hydrogen uptake, H_{ad}, is the difference between the total and the reversible uptakes, and it represents H chemisorbed on the Pd surface because no irreversible adsorption occurs on the support and absorption of hydrogen into Pd is reversible (*14, 15*). The H_{ab}/Pd_b ratio was calculated assuming that all the hydrogen reversibly adsorbed is associated with the β-hydride phase. This is reasonable for poorly dispersed catalysts, but on highly dispersed Pd catalysts the amount of reversible chemisorption on Pd becomes significant compared to the amount of β-hydride, and this can produce ratios higher than the expected values of 0.5–0.7 (*7, 8*). The surface-weighted average Pd crystallite size, *d*, was computed by the formula (*20*)

$$d(\text{nm}) = 1.13/D.$$

Kinetic Experiments

The hydrogenation of toluene and *ortho*-, *meta*-, and *para*-xylene gave the saturated cycloparaffin as the only detectable product—methylcyclohexane (MCH), 1,2-di-

TABLE 1

Characterization of Fresh Palladium Catalysts by H_2 Chemisorption

Catalyst	T_r (K)	H_2 uptake (μmol/g cat)		Dispersion $\left[\frac{H_{ad}}{Pd_t}\right]$	$\left[\frac{H_{rev}}{Pd_b}\right]$	d, Pd crystallite size (nm)
		Irrev	Rev			
Pd powder[a]	573	6.0	—	0.0013	—	940
1.3% Pd/MgO	448	15.0	24.5	0.25	0.54	4.5
2.67% Pd/SiO_2	673	69.9	14.0	0.56	0.25	2.0
0.25% Pd/Al_2O_3	673	5.7	3.8	0.48	0.61	2.4
0.5% Pd/Al_2O_3	673	11.1	4.7	0.44	0.33	2.6
1.1% Pd/TiO_2	673	11.0	17.6	0.21	0.45	5.4[b]
1.1% Pd/TiO_2	448	29.2	31.3	0.56	1.42	2.0
1.1% Pd/TiO_2	393	18.0	45.8	0.35	1.43	3.2
1.1% Pd/SiO_2–Al_2O_3	673	13.0	12.0	0.25	0.31	4.5
1.1% Pd/SiO_2–Al_2O_3	448	17.3	9.9	0.33	0.29	3.4
1.1% Pd–SiO_2–Al_2O_3	393	25.0	10.6	0.48	0.39	2.4

[a] Measured in the presence of α-hydride phase [16].
[b] Apparent value.

methylcyclohexane (2-DMC), 1,3-dimethylcyclohexane (3-DMC), and 1,4-dimethylcyclohexane (4-DMC), respectively. Some isomerization of *o*-xylene to *m*-xylene was observed, with the latter subsequently hydrogenating to give 3-DMC. No other isomerization reaction was observed.

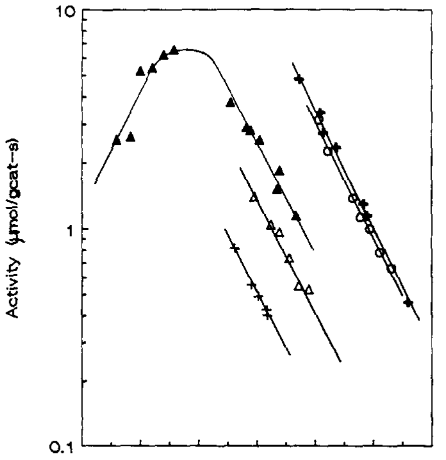

FIG. 1. Arrhenius plots for toluene hydrogenation over Pd catalysts at 680 Torr hydrogen, and 50 Torr toluene; 2.67% Pd/SiO_2 (393 K), ▲; 1.3% Pd/MgO (448 K), +; 1.1% Pd/SiO_2–Al_2O_3 (393 K), +; 1.1% Pd/SiO_2 Al_2O_3 (448 K), ○; 1.1% Pd/SiO_2–Al_2O_3 (673 K), △.

Toluene Hydrogenation

The specific activities, activation energies, and turnover frequencies (TOFs) are listed in Table 2, and a typical set of Arrhenius plots for this reaction is shown in Fig. 1. Benzene hydrogenation on Pd exhibits a reversible maximum near 495 K in such plots (*7, 8, 21*), and similar behavior has been reported for toluene (*21, 22*). As shown by the 2.67% Pd/SiO_2 catalyst in Fig. 1, under our reaction conditions the toluene hydrogenation rate passes through a maximum near 470 K. The highest activities are achieved with the most acidic supports, but their inertness in the absence of Pd, even after Cl impregnation, is clearly evident.

Xylene Hydrogenation

The results of the kinetic experiments on *o*-xylene hydrogenation to 2-DMC are shown in Table 3. Well-behaved Arrhenius plots were again routinely obtained (*17*), and turnover frequencies at 413K were up to an order of magnitude lower than those for toluene on the comparable catalyst. This re-

TABLE 2

Toluene Hydrogenation to Methylcyclohexane (MCH) over Pd Catalysts

Reaction conditions:
413 K, 50 Torr toluene, and 680 Torr H_2

Catalyst	T_r (K)	E $\left[\frac{\text{kcal}}{\text{mol}}\right]$	Activity		TOF[a] ($s^{-1} \times 10^3$)
			$\left[\frac{\mu\text{mol MCH}}{\text{s} \cdot \text{g cat}}\right]$	$\left[\frac{\mu\text{mol MCH}}{\text{s} \cdot \text{g Pd}}\right]$	
Pd powder	573	10.8	0.38	0.38	34
1.3% Pd/MgO	448	12.3	0.45	35	15
2.67% Pd/SiO_2	673	8.0	2.5	94	18
2.67% Pd/SiO_2	673	10.8	2.6	104	18
0.25% Pd/Al_2O_3	673	6.9	0.27	108	25
1.5% Pd/Al_2O_3	673	11.8	1.1	72	44
0.5% Pd/Al_2O_3	673	13.2	0.62	116	28
1.1% Pd/TiO_2	673	11.3	1.9	172	87
1.1% Pd/TiO_2	448	11.9	11.2	1018	191
1.1% Pd/TiO_2	393	12.8	3.9	354	108
1.1% Pd/SiO_2–Al_2O_3	393	12.6	8.7	790	173
1.1% Pd/SiO_2–AlO_2O_3	448	12.2	7.1	645	204
1.1% Pd/SiO_2–Al_2O_3	673	11.2	0.91	83	35
TiO_2[b]	448	—	0.0	—	—
SiO_2–Al_2O_3[b]	448	—	0.0	—	—

[a] Based on H_2 chemisorption on fresh catalysts.

[b] Impregnated with HCl.

action was complicated by the isomerization of *o*-xylene to the more thermodynamically stable *m*-xylene, a reaction known to occur under these conditions (*23*), and its rate was strongly dependent on the support acidity, as shown later.

m-Xylene is the most thermodynamically stable of the three isomers and it hydrogenates to 3-DMC in a pattern very similar to that of the other aromatics, with TOFs that are higher than those for *o*-xylene and lower than those for toluene. The results are tabulated in Table 4. No isomerization of *m*-xylene was observed nor was any activity detected for hydrogenation or isomerization over the HCl-impregnated TiO_2 and SiO_2–Al_2O_3 samples.

The results for the hydrogenation of *p*-xylene to 4-DMC are given in Table 5. TOF values for *p*-xylene were the highest among the xylenes and comparable to those for toluene on the catalysts that had no acidic support, which may be due to its symmetric structure (*19, 24*). The highest activation energies among benzene, toluene, and the three xylenes were obtained in this reaction. No isomerization to either *m*-xylene or *o*-xylene was observed.

Dependencies of Hydrogenation Activity on Partial Pressure

The results of the partial pressure study over the 0.5% Pd/Al_2O_3 and 1.1% Pd/SiO_2–Al_2O_3 catalysts are summarized in Table 6, and Figs. 2 and 3 show typical log–log plots of activity vs pressure. These two catalysts represented one of the least active and the most active samples. Despite the significant difference in the activities of the catalysts, both reaction orders with respect to H_2 were near unity, and with respect to the aromatic hydrocarbons were zero order above 20 Torr, with the exception of toluene over 1.1% Pd/SiO_2–Al_2O_3, which required

TABLE 3

o-Xylene Hydrogenation to 1,2-Dimethylcyclohexane (2-DMC) over Pd Catalysts

Reaction conditions:
413 K, 50 Torr o-xylene, and 680 Torr H_2

Catalyst	T_r (K)	E $\left[\frac{\text{kcal}}{\text{mol}}\right]$	Activity		TOF[a] ($s^{-1} \times 10^3$)
			$\left[\frac{\mu\text{mol 2-DMC}}{\text{s} \cdot \text{g cat}}\right]$	$\left[\frac{\mu\text{mol 2-DMC}}{\text{s} \cdot \text{g Pd}}\right]$	
Pd powder	573	15.1	0.055	0.055	4.9
1.3% Pd/MgO	448	7.4	0.13	10.0	4.3
2.67% Pd/SiO_2	673	13.4	0.35	13.1	2.5
0.5% Pd/Al_2O_3	673	14.9	0.07	13.2	3.2
1.1% Pd/TiO_2	673	14.2	0.16	14.5	7.2
1.1% Pd/TiO_2	448	13.8	1.18	107.0	20
1.1% Pd/SiO_2–Al_2O_3	448	10.4	0.69	63.1	20
TiO_2[b]	448	—	0.0	—	—
SiO_2–Al_2O_3[b]	448	—	0.0	—	—

[a] Based on H_2 chemisorption on fresh catalysts.
[b] Impregnated with HCl.

higher toluene pressures to achieve zero-order dependence (*17*). The solid lines in Figs. 2 and 3 represent the predicted rates obtained from the best fit provided by the Langmuir model discussed elsewhere (*10*).

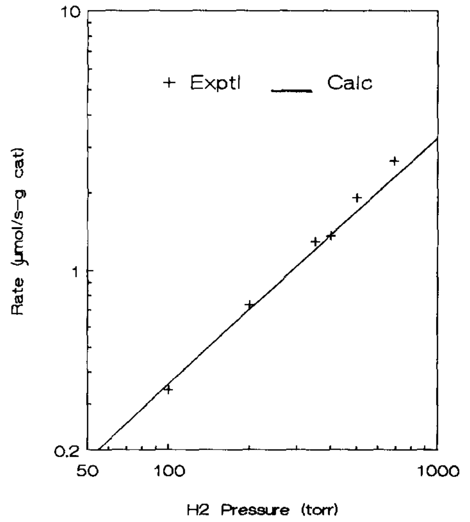

FIG. 2. Activity vs hydrogen partial pressure for m-xylene hydrogenation over 1.1% Pd/SiO_2–Al_2O_3 (448 K) at 413 K and 50 Torr m-xylene.

o-Xylene Isomerization

This reaction occurred in parallel with the hydrogenation reaction, and it provided an internal probe of the role of acid sites on the support. No isomerization was detected other than o-xylene to m-xylene, and this reaction occurred on all the Pd catalysts as well as the Cl-impregnated TiO_2 and SiO_2–Al_2O_3 alone. The amount of HCl added to the pure supports corresponded to the Cl concentration present after impregnation of $PdCl_2$. The rates of isomerization are given in Table 7.

DISCUSSION

The adsorption and hydrogenation of benzene on group VIII metals have been the subject of many investigations, yet there is still debate about the modes of adsorption and the reaction mechanism. The reviews on benzene chemisorption by Moyes and Wells (*25*) and by Garnett (*26*) give a thorough discussion of this subject. Numerous studies have been carried out on benzene hydrogenation using a variety of supports and metal precursor compounds, and this

TABLE 4

m-Xylene Hydrogenation to 1,3-Dimethylcyclohexane (3-DMC) over Pd Catalysts

Reaction conditions:
413 K, 50 Torr *m*-xylene, and 680 Torr H_2

Catalyst	T_r	E	Activity		TOF[a]
	(K)	$\left[\frac{\text{kcal}}{\text{mol}}\right]$	$\left[\frac{\mu\text{mol 3-DMC}}{\text{s} \cdot \text{g cat}}\right]$	$\left[\frac{\mu\text{mol 3-DMC}}{\text{s} \cdot \text{g Pd}}\right]$	($s^{-1} \times 10^3$)
Pd powder	573	11.4	0.30	0.30	27
1.3% Pd/MgO	448	12.4	0.45	35	15
2.67% Pd/SiO_2	673	11.5	2.10	79	15
0.5% Pd/Al_2O_3	673	14.2	0.33	62	13
1.1% Pd/TiO_2	673	11.5	0.67	62	30
1.1% Pd/TiO_2	448	11.3	3.48	316	59
1.1% Pd/SiO_2–Al_2O_3	448	12.0	2.05	186	57
TiO_2[b]	448	—	0.0	—	—
SiO_2–Al_2O_3[b]	448	—	0.0	—	—

[a] Based on H_2 chemisorption on fresh catalysts.
[b] Impregnated with HCl.

reaction has been used as a probe to gain insight into metal-support effects and the influence of structure on catalytic properties (*3–9, 21, 27–31*). Recently there has been an effort to employ toluene hydrogenation as a probe reaction to supplement the present understanding of benzene hydrogenation and, to some extent, to confirm conclusions related to the latter reaction. However, much less experimentation has been carried out on toluene hydrogenation.

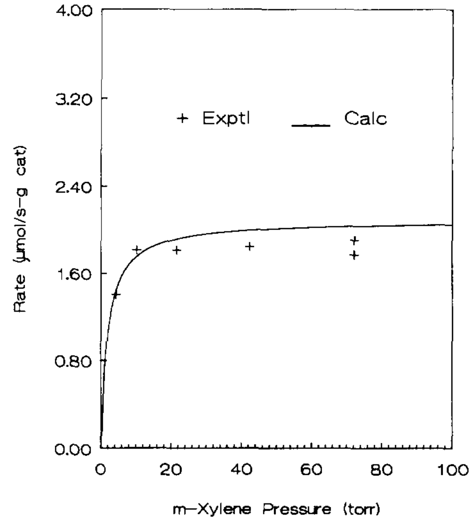

FIG. 3. Activity vs *m*-xylene partial pressure for *m*-xylene hydrogenation over 1.1% Pd/SiO_2–Al_2O_3 (448 K) at 413 K and 600 Torr hydrogen.

Rader and Smith investigated the kinetics of polymethylbenzenes over platinum oxide in acetic acid solution and carried out a number of competitive hydrogenations to estimate the ratios of equilibrium adsorption constants for different pairs of polymethylbenzenes (*19*). Orozco and Webb investigated toluene hydrogenation and the competitive hydrogenation of benzene and toluene over Pt and Pd supported on silica and alumina (*21*). Massardier and coworkers have also used the competitive hydrogenation of benzene and toluene to obtain ratios of equilibrium adsorption constants, K_T/K_B, to probe the electronic structure of group VIII metals (*32, 33*). Rabette *et al.* used toluene hydrogenation to study the catalytic properties of Pt^+ ions implanted on single crystal supports (*34*), and this reaction over Pt and Pt–Cu alloys was used by Bandiera and Meriaudeau to help character-

TABLE 5

p-Xylene Hydrogenation to 1,4-Dimethylcyclohexane (4-DMC) over Pd Catalysts

Reaction conditions:
413 K, 50 Torr *p*-xylene, and 680 Torr H_2

Catalyst	T_r (K)	E $\left[\frac{\text{kcal}}{\text{mol}}\right]$	Activity $\left[\frac{\mu\text{mol 3-DMC}}{\text{s}\cdot\text{g cat}}\right]$	Activity $\left[\frac{\mu\text{mol 3-DMC}}{\text{s}\cdot\text{g Pd}}\right]$	TOF[a] ($s^{-1} \times 10^3$)
Pd powder	573	14.4	0.56	0.56	50
1.3% Pd/MgO	448	17.1	0.42	32	14
2.67% Pd/SiO_2	673	14.7	2.79	104	20
0.5% Pd/Al_2O_3	673	13.7	0.29	54	14
1.1% Pd/TiO_2	673	12.0	0.60	55	27
1.1% Pd/TiO_2	448	14.3	7.33	663	124
1.1% Pd/SiO_2–Al_2O_3	448	12.5	3.06	278	88

[a] Based on H_2 chemisorption on fresh catalysts.

ize this bimetallic system (*22*). The liquid-phase hydrogenation kinetics of toluene over Ru, Pd, and Pt catalysts have also been studied (*35, 36*). There have also been several spectroscopic and TPD studies of toluene adsorption on metal surfaces (*37–42*). The results from these previous investigations of toluene are summarized in Table 7. Only two studies have provided turnover frequencies for this reaction, and no steady-state values are available for Pd because a pulse reactor was utilized by Orozco and Webb (*21*).

TABLE 6

Reaction Orders with Respect to H_2 and Aromatic Compounds for Hydrogenation over Pd

Rate = $kP_A^X P_{H_2}^Y$
Total pressure = 730 Torr

Aromatic compound, A	Catalyst Pd/Al_2O_3 X^a	Pd/Al_2O_3 Y^b	Pd/SiO_2–Al_2O_3 (448 K) X^a	Pd/SiO_2–Al_2O_3 (448 K) Y^b
Benzene[c]	0.0	0.9	0.0	1.0
Toluene[d]	0.0	1.3	0.0	1.1
o-Xylene[e]	0.0	1.1	0.0	1.1
m-Xylene[e]	0.0	1.1	0.0	1.1

[a] Determined at 50 Torr of aromatic hydrocarbon.

[b] Determined at 600 Torr H_2.

[c] T_{rxn} = 413 K from Ref. (*8*).

[d] T_{rxn} = 363 K for Pd/SiO_2–Al_2O_3 and 413 K for Pd/Al_2O_3.

[e] T_{rxn} = 438 K for Pd/Al_2O_3 and 413 K for Pd/SiO_2–Al_2O_3.

A comparison of our results with this prior work reveals some differences but much consistency. The only previous investigation of toluene hydrogenation over Pd, that of Orozco and Webb (*21*), reports much lower activation energies of 4–6 kcal/mol. The use of a pulse reactor coupled with high conversions (10–90%) may have introduced diffusional effects. They also reported that TOFs for toluene hydrogenation over Pd/Al_2O_3 were higher than those for benzene hydrogenation while over Pd/SiO_2 the opposite trend was true. The result with Pd/Al_2O_3 does not agree with the results of the present study, nor do the TOF values for toluene hydrogenation agree well as they are 4–9 times higher than those in Table 2. This may be due to the difficulties associated with the use of a pulse reactor for a zero-order reaction (*31*).

Fujie *et al.* studied the promoting effect

TABLE 7

o-Xylene Isomerization to *m*-Xylene over Pd Catalysts and Supports Alone

Reaction conditions:
413 K, 50 Torr *o*-xylene, and 680 Torr H_2

Catalyst	T_r (K)	Activity		TOF[a] ($s^{-1} \times 10^3$)
		$\frac{\mu\text{mol } m\text{-Xyl}}{\text{s} \cdot \text{g cat}}$	$\frac{\mu\text{mol } m\text{-Xyl}}{\text{s} \cdot \text{g Pd}}$	
Pd powder	573	0.055	0.055	4.9
1.3% Pd/MgO	448	0.13	10.0	4.4
2.67% Pd/SiO_2	673	0.75	28.0	5.4
0.5% Pd/Al_2O_3	673	0.15	28.0	6.8
1.1% Pd/TiO_2	673	0.25	22.0	11
1.1% Pd/TiO_2	448	1.42	183	24
1.1% Pd SiO_2–Al_2O_3	448	0.83	75	24
TiO_2[b]	448	0.18	—	—
SiO_2–Al_2O_3	448	0.04	—	—

[a] Based on H_2 chemisorption [11].

[b] Impregnated with dilute HCl.

of BaO on benzene and toluene hydrogenation over Ni/Al_2O_3 (*27*). They found that as the BaO content increased, H_2 uptakes also increased proportionally, indicating that the effect of BaO was merely to increase metal dispersion. The TOF for toluene hydrogenation was 0.10 s^{-1} at 413 K, which seems reasonable because Ni is more active than Pd for hydrogenation. Also, the TOFs for benzene hydrogenation were consistently higher than those for toluene.

Activation energies for toluene hydrogenation have been reported in several studies. Bandiera and Meriaudeau obtained activation energies of 12 kcal/mol and 16 kcal/mol over Pt/NaY and Pt–Cu/NaY, respectively (*22*). They found that the bimetallic catalysts had much lower activity compared to Pt/NaY, which is consistent because Cu is virtually inactive for hydrogenation due to its filled *d*-band. Rabette *et al.* employed toluene hydrogenation to characterize Pt^+ ions implanted on single crystals of Al_2O_3 and MgO, and on both catalysts they observed an activation energy of 11.0 kcal/mol (*34*). They also reported that substantially greater rates were observed when the catalysts were pretreated in O_2 rather than in H_2; however, they did not measure TOFs. Experiments on pure alumina yielded no product. Völter *et al.* reported activation energies for toluene hydrogenation between 363 and 473 K over Ni/MgO, Rh/MgO, and Co/MgO of 13.5, 7.4, and 13.1 kcal/mol, respectively (*43, 44*). More recently, Hanika *et al.* reported a H_2 reaction order of unity at 345 K over Pt/SiO_2 and a low activation energy of 5.0 kcal/mol (*35*), which again introduces a concern of diffusional effects. The study by Konyukhov *et al.* found a zero-order dependence on toluene over Pd/C at 543 K, but gave no activities (*36*).

Even fewer studies exist for xylene hydrogenation, and no TOFs have been reported; however, some limited information is available. Aramendia *et al.* have investigated the vapor-phase hydrogenation of the xylene isomers over four supported Pd catalysts using a pulse reactor, but only conversions were reported (*45*). Over all the catalysts, conversions increased in the order: *o*-xylene < *m*-xylene < *p*-xylene, a trend which agrees with our data as well as those of Rader and Smith, who reported hydrogenation rate constants for *o*-, *m*-, and *p*-xylene of 0.091, 0.126, and 0.158 liter $H_2 \cdot min^{-1}$ g cat^{-1} over PtO at 303 K and 345 kPa H_2 (*19*). Smith and Pennekamp have reported reaction orders of unity for H_2 and zero for these aromatics over a Pt catalyst (*24*). Harper and Kemball investigated both deuterium exchange and hydrogenation of *p*-xylene on Pd, W, and Pt, but reported no specific activities (*46*). These results are also listed in Table 8.

Toluene

The results in Table 2 and Fig. 4 show a marked influence of the support and the reduction temperature on the TOFs for toluene hydrogenation. Benzene hydrogenation has been used as a probe reaction to study support effects in these types of catalyst because the reaction is essentially structure-insensitive (*2–5*), and reported TOF values for benzene hydrogenation over metals on typical supports like silica, alumina, and magnesia exhibit little variation; however, Pd catalysts utilizing acidic supports such as SiO_2–Al_2O_3 or zeolites have exhibited much higher TOFs (*3–8*). Thus analogous behavior is observed for toluene hydrogenation. After reduction at 673 K, TOF values for the Pd/SiO_2, Pd/Al_2O_3, Pd/MgO, and Pd powder catalysts were 0.025 ± 0.010 s^{-1}. However, Pd/TiO_2 (673 K) had a higher TOF of 0.087 s^{-1}, and for the Pd/SiO_2–Al_2O_3 and Pd/TiO_2 catalysts after a low-temperature reduction at 448 K, the average TOF of 0.198 s^{-1} was 8 times higher than the average TOF value for the nonacidic catalysts. However, despite large differences in activities, supports, and reduction temperatures, the activation energy remained essentially constant at 11.8 ± 1.0 kcal/mol, which is comparable to that for benzene hydrogenation on these catalysts (*7*).

For the acidic Pd/SiO_2–Al_2O_3 and Pd/TiO_2 catalysts, the reduction temperature also had an effect on TOF values, and as it was lowered from 673 to 448 K six-fold and three-fold increases in TOF values occurred for the Pd/SiO_2–Al_2O_3 and Pd/TiO_2 samples, respectively. Similar behavior was observed for benzene hydrogenation (*7, 8*). This increase in TOF cannot be attributed to changes in crystallite size because little or no sintering occurred and all average crystallite sizes remained between 2 and 7 nm. Viniegra *et al.* have reported that benzene hydrogenation activity on Ru/MgO was about two orders of magnitude higher than either Ru/SiO_2 or Ru/SiO_2-Al_2O_3 (*47*); however, such an activity increase over Pd/MgO for either benzene or toluene hydrogenation was not observed in our study. The TOF for either benzene (29×10^{-3} s^{-1}) or toluene (15×10^{-3} s^{-1}) over Pd/MgO was comparable to the respective TOF over Pd powder, suggesting the absence of any influence of MgO on activity. Possible explanations of this behavior have been listed elsewhere (*7, 8*) and are discussed subsequently (*10*).

The kinetics of toluene hydrogenation appear to be similar to benzene hydrogenation in many respects (*8, 9, 21*), and a careful comparison between the results reported here and those from our recent study of benzene hydrogenation over Pd reveals strikingly similar behavior. For example, the activation energies are nearly the same as are the partial pressure dependencies in Table 6. In addition, the activity for toluene hydrogenation over Pd/SiO_2 passes through a maximum near 470 K as the temperature is increased (see Fig. 1). This behavior agrees with previous work (*21, 22*), and it is similar to the maximum found for benzene hydrogenation (*7, 8, 21*). The maxima for both benzene and toluene are reversible and can be traversed from either the high- or low-temperature side, which implies that they are not due to catalyst deactivation. Also, they are not a consequence of thermodynamic limitations because the conversions were far from equilibrium conversions. The occurrence of this maximum for benzene has been explained by the continued decrease in the aromatic hydrocarbon surface coverage as

TABLE 8

Kinetic Parameters for Benzene, Toluene, and Xylene Hydrogenation from Previous Studies

Catalyst	T (K)	P_{H2} (Torr)	P_A (Torr)	Activity (μmol/μmol Me · s)	TOF (s^{-1})	E_a (kcal/mol)	Conv. (%)	Ref.
Benzene hydrogenation								
Pd Powder	413	680	50	5×10^{-5}	0.040	11.2	<15%	17[a]
Pd/SiO_2	413	680	50	0.022	0.040	11.3	<15%	17
Pd/Al_2O_3	413	680	50	0.018	0.040	13.1	<15%	17
Pd/MgO	413	680	50	0.007	0.029	11.5	<15%	17
Pd/TiO_2 (T_r = 448 K)	413	680	50	0.010	0.104	12.3	<15%	7,8[a]
Pd/TiO_2 (T_r = 673 K)	413	680	50	0.007	0.463	11.9	<15%	7,8
$Pd/SiO_2–Al_2O_3$ (T_r = 448 K)	413	680	50	0.39	1.112	14.2	<15%	7,8
Toluene hydrogenation								
Pd/SiO_2	413	—	—	0.0077	0.155	6.0	10–90	21[b]
Pd/Al_2O_3	413	—	—	0.0065	0.130	4.2	10–90	21
Pt/SiO_2	413	—	—	0.5480	10.5	6.0	10–90	21
Pt/Al_2O_3	413	—	—	0.608	11.0	6.0	10–90	21
Pt/NaY	413	—	—	0.0045	—	12.0	low	22[a]
Pt–Cu/NaY				0.7×10^{-4}	—	16.0	low	22
Pt/α-Al_2O_3	466	500	50	0.2×10^{-4}	—	11.0	low	34[a]
Pt/MgO	466	500	50	0.3×10^{-4}	—	11.0	low	34
α-Al_2O_3	466	500	50	0.0	—	—	—	34
Pt/SiO_2	345	—	—	—	—	5.0	—	35[c]
Ni/Al_2O_3	413	570	190	0.8×10^{-2}	0.10	—	low	27[a]
Ni/MgO	363–473	—	—	—	—	13.5	—	43
Rh/MgO	363–473	—	—	—	—	7.4	—	44
Co/MgO	363–473	—	—	—	—	13.1	—	44
Xylene hydrogenation								
o-Xylene								
PtO	303	1840	—	0.097[d]	—	—	low	19[c,e]
m-Xylene								
PtO	303	1840	—	0.126[d]	—	—	low	19[c,e]
p-Xylene								
PtO	303	1840	—	0.158[d]	—	—	low	19[c,e]
Ni/MgO	363–473	—	—	—	—	11.1	—	43
Rh/MgO	363–473	—	—	—	—	8.7	—	44
Co/MgO	363–473	—	—	—	—	14.2	—	44

[a] Differential flow reactor.
[b] Pulse reactor.
[c] Liquid-phase hydrogenation.
[d] 1 H_2/min-g cat.
[e] Batch reactor.

temperature increases, which at some point becomes small enough to noticeably decrease the rate (*8*, *9*). A similar explanation for toluene seems appropriate based on Fig. 1 and the nearly identical reaction orders shown in Table 6.

As mentioned previously, Table 2 shows that Pd/SiO_2-Al_2O_3 and Pd/TiO_2 can be much more active than Pd powder, Pd/SiO_2, Pd/MgO, or Pd/Al_2O_3. This activity pattern is the same as that found for benzene hydrogenation on the same Pd catalysts (*7*, *8*), but there are no earlier investigations of toluene hydrogenation to which to compare. The

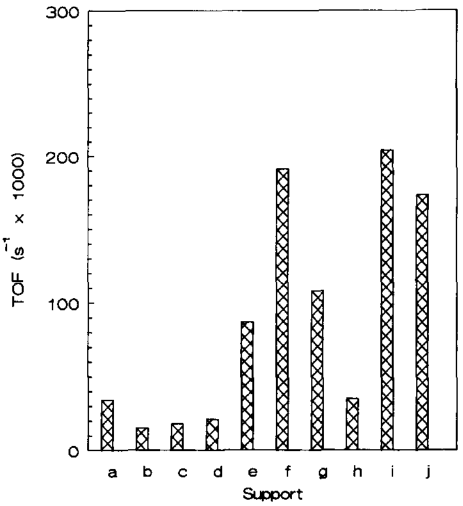

FIG. 4. Influence of the support on toluene hydrogenation over palladium catalysts at 413 K, 680 Torr hydrogen, and 50 Torr toluene: (a) None; (b) MgO; (c) SiO_2; (d) Al_2O_3; (e) TiO_2 (673 K); (f) TiO_2 (448 K); (g) TiO_2 (393 K); (h) SiO_2–Al_2O_3 (673 K); (i) SiO_2–Al_2O_3 (448 K); (j) SiO_2–Al_2O_3 (393 K).

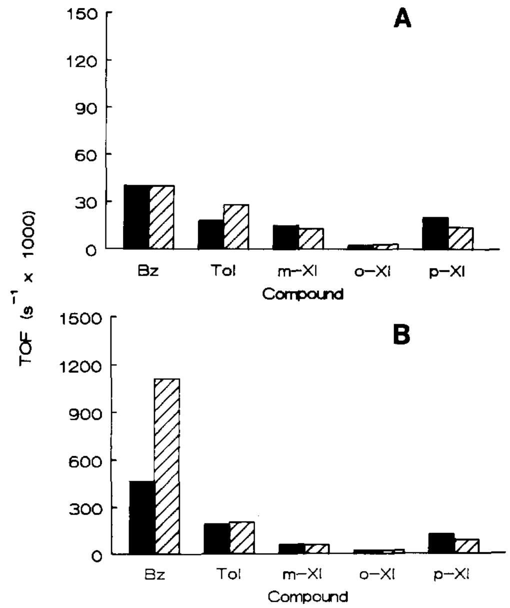

FIG. 5. Turnover frequencies for the hydrogenation of aromatic hydrocarbons at 413 K, 50 Torr aromatic compound, and 680 Torr hydrogen: Benzene, Bz; toluene, Tol; *m*-xylene, *m*-Xl; *o*-xylene, *o*-Xl; *p*-xylene, *p*-Xl. (A) Pd/SiO_2, solid bars; Pd/Al_2O_3, striped bars. (B) Pd/TiO_2 (448 K), solid bars; Pd/SiO_2–Al_2O_3 (448 K), striped bars.

TOF for toluene hydrogenation increases with the acidity of the support, as indicated by the comparison in Fig. 4. Basic or inert supports have no positive effect on the TOF whereas Pd on SiO_2–Al_2O_3 or TiO_2 reduced at low temperature, which would have the most Cl and the highest Brønsted acid site concentration on the surface, has TOF values that are much higher. A reduction at 673 K, which removes Cl and decreases the number of Brønsted sites, markedly reduces TOF values. The somewhat lower TOFs after reduction at 393 K may be due to incomplete reduction of the Pd. Although charge transfer to the support to give electron-deficient Pd particles has been proposed for benzene hydrogenation (*6*), this explanation has been discounted because of the relatively large Pd crystallites present in these catalysts (*7, 8*). In addition, based on the arguments of Massardier and co-workers (*32, 33*), toluene adsorption on electron-deficient Pd might be expected to be stronger than on zero-valent Pd, and since the surface is nearly saturated already, a decrease in activity might be anticipated, rather than an increase. Finally, if Pd dispersed on nonacidic oxides is compared to Pd powder, the TOF values vary by only a factor of two while crystallite sizes range from 2 to 940 nm. This demonstrates that toluene hydrogenation is structure-insensitive, as anticipated based on previous studies of benzene hydrogenation.

A comparison of TOF values for hydrogenation of toluene and benzene over Pd dispersed on acidic and nonacidic supports, shown in Fig. 5, illustrates that toluene hydrogenates at a lower rate than benzene over any given catalyst. The lower TOFs for toluene might be anticipated because toluene has a greater stability than benzene due to the increased electron density of the π-electron cloud (*48*). The ratio of toluene to benzene hydrogenation TOFs is higher (0.5–0.9) in the absence of an acidic support than in the presence of one (0.2–0.4). On the latter catalysts, a majority of the overall rate is presumed to come from a contribution due to acidic sites in the Pd-support interface region that provide additional adsorption sites (*8*). Although no direct data are available, it has been assumed that toluene adsorbed on transition metals has a greater bond strength than benzene and that the relative bond strength increases as electron deficiency of the adsorption site increases (*21, 32, 33*). If so, toluene might be expected to bond even more strongly to an acid site than on a metal surface. However, Gallezot *et al.* have reported kinetically derived K_T/K_B ratios near unity for Pd, in good agreement with the ratio obtained with our K_T and K_B values for Pd/Al_2O_3 (*10*), implying similar bond strength. Thus a stronger interaction between toluene and an acidic site, compared to benzene, could reduce the reaction rate on the oxide and hence decrease the relative contribution from the interface region.

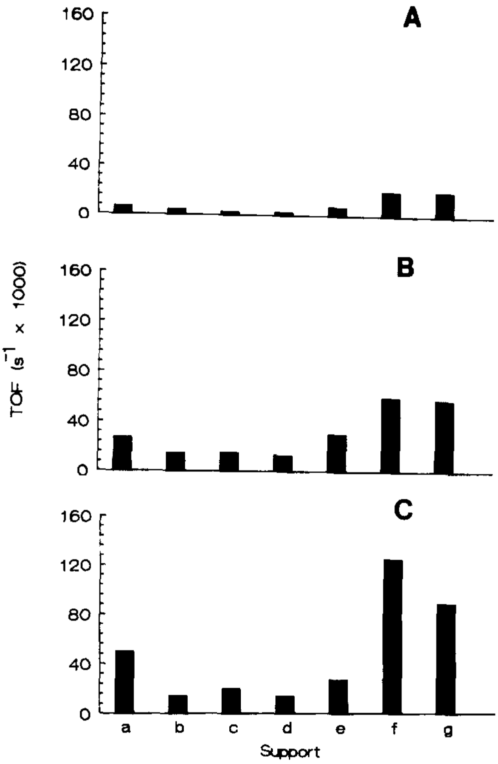

FIG. 6. Influence of the support on xylene hydrogenation over palladium catalysts at 413 K, 680 Torr hydrogen, and 50 Torr xylene: (a) None; (b) MgO; (c) SiO_2; (d) AlO_3; (e) TiO_2 (673 K); (f) TiO_2 (673 K); (g) SiO_2–Al_2O_3 (448 K). (A) *o*-xylene. (B) *m*-xylene. (C) *p*-xylene.

The Xylenes

The data for the hydrogenation of *o*-xylene (Table 3), *m*-xylene (Table 4), and *p*-xylene (Table 5) show again that the support can influence TOF values. However, as illustrated in Fig. 6, for each xylene isomer the TOF is less dependent on the support compared to benzene or toluene although the observed pattern is very similar. Over any given Pd catalyst the TOF values for hydrogenation of the xylene isomers increased in the order: *ortho* < *meta* ≤ *para*. The hydrogenation rates for *o*-xylene were 4–6 times lower than for *m*-xylene, and the latter hydrogenated at comparable or slightly lower rates than *p*-xylene over a particular catalyst. For Pd powder, Pd/SiO_2, Pd/Al_2O_3, Pd/MgO, and Pd/TiO_2 (673 K) the TOF values were 0.005 ± 0.002 s^{-1} for *o*-xylene, 0.022 ± 0.008 s^{-1} for *m*-xylene, and 0.032 ± 0.018 s^{-1} for *p*-xylene. Pd/TiO_2 reduced at 673 K had a hydrogenation TOF comparable to that of Pd powder, while the Pd/SiO_2–Al_2O_3 and Pd/TiO_2 samples reduced at 448 K had higher TOFs compared to the other catalysts, but the enhancement depended somewhat on the isomer. The *o*-xylene activity on these acidic catalysts was 5 times higher than the nonacidic samples, while for *m*-xylene and *p*-xylene it was 3–4 times that of the samples with nonacidic supports. With one exception, activation energies for the hydrogenation of the three xylenes fell in the range of 11–15 kcal/mol, irrespective of the support and the reduction temperature. They increased in the order: *meta-* < *ortho-* < *para*xylene as the average values were 12.0 ± 0.7 kcal/mol, 12.7 ± 2.0 kcal/mol, and 13.7 ± 1.7 kcal/mol, respectively. For xylene hydrogenation over Pd/TiO_2 the reduction temperature had the same effect as that observed for toluene and benzene hydrogenation; that is, a lower temperature of 473 K rather than 673 K produced two- to fourfold increases in the activity. The similarity in activation energies and the partial pressure dependencies in Table 6 imply a very similar reaction sequence for all five aromatic hydrocarbons. Thus the explanation for this enhancement in the TOF because of the acidic support is the same as that proposed for benzene (*7–9*) and toluene; i.e., acidic sites present in the metal-support interfacial region also adsorb the aromatic which is hydrogenated by hydrogen spilling over from the Pd crystallites (*9*).

A further examination of Fig. 5 reveals an important result of the present study. The relative hydrogenation rates among this family of aromatic hydrocarbons can be significantly altered by the choice of support and pretreatment. With the most acidic supports, the hydrogenation of benzene, and also toluene to a lesser extent, is enhanced much more than the hydrogenation of the xylenes. With nonacidic supports, the relative rates are much more similar, and with Pd powder there is little difference at all, except for the somewhat lower rate for *o*-xylene.

The addition of methyl groups to the benzene ring can introduce both electronic and steric effects. Although it is not easy to separate these two contributions based on the kinetic results alone, some conclusions may be drawn. First, the rate of toluene hydrogenation is always less than that for benzene on a particular catalyst, yet UHV spectroscopic studies of these two molecules on Pt and Pd (*37–40*) show very similar, π-bonded surface species although coordination via the methyl group has also been suggested (*41, 42*). Thus this activity decrease appears to be attributable to an electronic effect. This conclusion is also consistent with the work of Phoung *et al.*, who reported equilibrium adsorption constants for benzene and toluene under reaction conditions on Pd (*33*). Second, *o*-xylene always has the lowest activity while the rates of *m*- and *p*-xylene are typically quite similar or only slightly lower than that for toluene hydrogenation over Pd on nonacidic supports. As the ionization potentials for *o*- and *m*-xylene are essentially the same (9.04 eV vs 9.05 eV, respectively), it is assumed that this is primarily a steric effect. Although no spectroscopic studies of xylene adsorption on metals have been reported, steric hindrance of neighboring methyl groups is routinely observed for *o*-xylene and this could have a significant effect on the formation of π-bonded complexes. Such constraints would be relaxed with the *meta*- and *para*-isomers. The absence of a significant decline in TOF for *m*- and *p*-xylene compared to toluene indicates that electronic effects are minimal. One complication in this comparison, however, is the concurrent isomerization of *o*-xylene to *m*-xylene which would reduce the surface coverage of the former isomer under reaction conditions (*10*).

Although the addition of methyl groups decreases the ionization potential (I.P.) in the order benzene (9.56 eV) > toluene (9.18 eV) > *m*-xylene (9.05 eV) ≥ *o*-xylene (9.04 eV) > *p*-xylene (8.99 eV) (*49*), there is no distinct effect on the activation energies. Thus we do not observe the decrease in E_{act} with decreasing I.P. as reported by Völter for polymethylbenzene hydrogenation over Ni/MgO (*43, 44*). However, Völter *et al.* did not find such a correlation with Co/MgO and Rh/MgO catalysts (*44*). The trend of average hydrogenation rates of toluene and *o*-, *m*-, and *p*-xylene in the absence of an acidic support, relative to that of benzene (0.63, 0.11, 0.47, and 0.65, respectively), is quite similar to that reported by Rader and Smith for these reactions over PtO in an acetic acid solution (0.72, 0.44, 0.61, and 0.77) (*19*). This implies that the reaction surface chemistry on these two metals is similar, as might be expected.

There are no previous studies of xylene isomerization over Pd to which these results can be compared. The isomerization of *o*-xylene to *m*-xylene by an acid-catalyzed, carbonium ion reaction is well known, and it has been used to estimate relative acid site concentrations on oxide surfaces (*50*). The results for the TiO_2 and SiO_2–Al_2O_3 samples verify that this reaction occurs readily over these acidic supports in the absence of Pd; however, the relatively low rates per gram compared to the Pd-containing catalysts were very likely due to poisoning of acid sites by the formation of coke precursors because significant deactivation occurred with time on stream. This deactivation was not observed for the catalysts with Pd, presumably because spilled-over hydrogen can react with these carbonaceous species and remove them. Such a role for hydrogen spillover has been proposed in Pt catalytic reforming catalysts (*51*). It is of some importance to note that the isomerization rate on the Pd surface alone was quite substantial and comparable to that for *o*-xylene hydrogenation and, in fact, on the Pd powder and Pd/MgO catalysts the rate of isomerization was identical to the rate of hydrogenation. Furthermore, these isomerization rates were independent of the use of a Cl-containing Pd precursor; thus chloride was not an important factor in this reaction. Consequently, unless protonic hydrogen exists on these Pd surfaces, an alternative reaction pathway other than that involving carbonium ion chemistry appears to exist on Pd itself. The isomerization activity showed little dependence on temperature; thus the activation energy for this reaction was very low. The isomerization rate was noticeably enhanced when Pd was dispersed on an acidic oxide support and it was clearly decreased on the Pd/TiO_2 catalyst after a high-temperature reduction. This pattern is fully consistent with the assumption that Brønsted acid sites are the principal active sites (*50*). This behavior verifies that *o*-xylene isomerization is indeed a good reaction to probe for the presence of acid sites, and the significance of this is discussed in the following paper (*10*).

SUMMARY

This study has shown that the trends found for benzene hydrogenation over this family of Pd catalysts are reproduced by toluene and xylene hydrogenation. The most acidic oxide supports, SiO_2–Al_2O_3 and TiO_2, give marked enhancements in specific activity, whereas MgO, SiO_2, and Al_2O_3 provide activities comparable to a high-purity Pd powder. For these five aromatic compounds, with either acidic or nonacidic supports, rates are first order in H_2 and zero order in the aromatic hydrocarbon at the partial pressures utilized, activation energies fall between 11 and 15 kcal/mol, and a reversible activity maximum occurs in Arrhenius plots. The highest activity always occurs with benzene and the lowest always with *o*-xylene, and the overall trend in TOFs is benzene $>$ toluene $\geq$ *p*-xylene $\geq$ *m*-xylene $>$ *o*-xylene. However, a proper choice of the support and the pretreatment can alter relative activities quite markedly; for example, the highest activities were always obtained by the low-temperature reduction of SiO_2–Al_2O_3 and TiO_2. Consequently, this capability may possibly be used to control selectivity during the hydrogenation of a mixture of these aromatic hydrocarbons. The kinetic model proposed for this system is described in the following paper (*10*).

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