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Hydrogenation of Aromatic Hydrocarbons over Supported Pt Catalysts

II. Toluene Hydrogenation

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Vapor-phase toluene hydrogenation was investigated over Pt supported on SiO_2, η-Al_2O_3, $SiO_2 \cdot Al_2O_3$, and TiO_2. As with benzene, activation energies and reaction orders had no dependence on the support. The E_A values were 12 ± 2 kcal/mol and the partial pressure dependence on toluene was near zero, i.e., essentially the same as for benzene; however, the H_2 pressure dependence increased from less than 0.7 at 333 K to over unity at 373 K. The turnover frequencies were four times higher with the most acidic support compared to the least acidic support, i.e., at 333 K under 50 Torr toluene and 685 Torr H_2, the TOF on 0.24% $Pt/SiO_2 \cdot Al_2O_3$ was 0.112 s^{-1}, whereas it was 0.027 s^{-1} on 0.96% Pt/SiO_2. This rate enhancement is attributed to an additional hydrogenation reaction occurring via hydrogen spilling over onto the support and reacting with aromatic molecules adsorbed on acid sites on the oxide. Deactivation was less of a problem with toluene compared to benzene. © 1993 Academic Press, Inc.

INTRODUCTION

The support used to disperse a metal can have a significant effect on the specific activity for hydrogenation of aromatic hydrocarbons; for example, turnover frequencies for benzene, toluene, and xylene hydrogenation over Pd were consistently higher with acidic supports such as silica–alumina than those with silica (*1*, *2*). It was proposed in these studies that acidic sites on the support material can act as adsorption sites for these aromatic compounds, and in the region surrounding a Pd particle these adsorbed species can react with hydrogen spilled over from the metal, thus contributing to the overall activity (*1*, *2*). To determine if similar behavior occurs with Pt catalysts, benzene and toluene hydrogenation over Pt dispersed on these same supports was investigated (*3*). The results for benzene hydrogenation are reported in the preceding paper (*4*), and this paper described the results for toluene hydrogenation.

EXPERIMENTAL

All the platinum catalysts, the pretreatments, the equipment, and the procedures were identical to those described previously (*3–7*). The toluene (Aldrich, HPLC grade, 99.9+%) was stored under He without further purification and fed to the preheater with a syringe pump (Sage Inst.). The vapor-phase hydrogenation of toluene (Tol) was studied between 333 and 373 K, and a bracketing technique using pure H_2 was used to minimize deactivation; however, loss of activity with time on stream was still observed in some cases. Conversions were typically below 12% and tests indicated that mass transfer limitations were absent. Toluene reaction orders were determined at 685 Torr H_2 and H_2 reaction orders were determined at 50 Torr toluene.

RESULTS

The temperature dependence of the toluene hydrogenation activity of these Pt cata-

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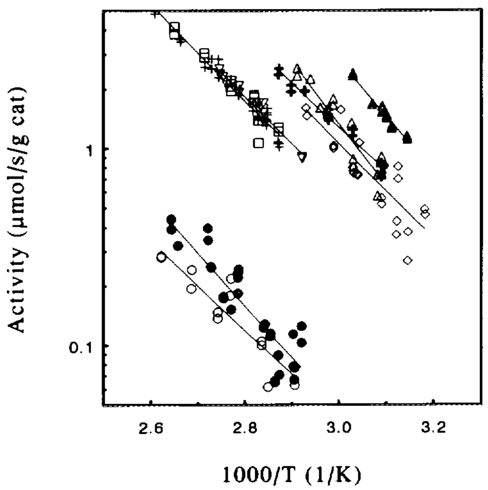

Fig. 1. Arrhenius plots of toluene hydrogenation over Pt catalysts at 50 Torr Tol and 685 Torr H_2: 0.96% Pt/SiO_2 (+), 0.95% Pt/TiO_2 (LTR) (▲), 0.95% Pt/TiO_2 (HTR) (△), 0.09% Pt/TiO_2 (LTR) (●), 0.09% Pt/TiO_2 (HTR) (○), and 0.24% $Pt/SiO_2 \cdot Al_2O_3$ reduced at 448 K (+), 673 K (□), and 723 K (▽).

lysts is shown in Fig. 1, and specific activities and activation energies are compared in Table 1. The Pt dispersions based on hydrogen chemisorption were reported in the previous paper (*4*). The activity of the Pt powder could not be accurately recorded because of its rapid deactivation. At Pt loadings above 0.2% the specific activity, i.e., the turnover frequency (TOF), follows the sequence $Pt/SiO_2 \cdot Al_2O_2 > Pt/TiO_2$ (LTR) $> Pt/Al_2O_3 \cong Pt/SiO_2$, thus it shows a trend similar to that found with supported Pd catalysts (*2*). The specific activity of Pt/SiO_2 and Pt/Al_2O_3 is consistent with the limited literature data in Table 2 obtained under constant feed conditions which could be expressed as TOF values. The exceptionally high TOFs found with the nonsteady-state pulse experiments are attributed to difficulties associated with this technique when applied to a zero-order reaction (*8*, *9*), and the low activation energies, which are about one-half the E_A values found in Table 1, are almost certainly due to pore diffusion effects. A reversible maximum activity near 463 K was observed in one run which was conducted over a wide temperature range, as shown in Fig. 2. The reduction temperature had little effect on the activity of the $Pt/SiO_2 \cdot Al_2O_3$ samples on a gram basis, but since the $H_{(ad)}/Pt$ ratio decreased as the reduction temperature increased, the apparent turnover frequency doubled after the highest reduction temperature. With the Pt/TiO_2 catalyst, the HTR sample had a lower activity than the LTR sample, which is consistent with the evidence that the "SMSI" state lowers the catalytic activity for most hydrogenation reactions due to coverage of the Pt surface sites by TiO_x species (*10*, *11*). The lower specific activity of the 0.09% Pt/TiO_2 catalyst compared to the 0.95% Pt/TiO_2 catalyst is attributed to a deactivation process because the activity of different samples varied noticeably; however, it could also be due to more complete coverage of the smaller amount of Pt by TiO_x species. Some deactivation was also observed in runs with other supported Pt catalysts, but its influence was minor. The activation energy does not seem to be significantly affected by either the type of support or the reduction temperature, and the average value is approximately 12 ± 2 kcal/mol, which is the same as that found for Pd catalysts (*2*).

The results of the studies with these Pt catalysts to determine reaction orders are shown in Fig. 3, where the error bars represent 95% confidence limits of the regressed reaction orders. Considering the Pt catalysts as a group, the reaction order on H_2 increases from below 0.7 at 333 K to over 1.0 at 373 K, whereas the reaction order on toluene is near zero at 333 K and increases only slightly up to 373 K. All the partial pressure plots are shown elsewhere (*3*), but two sets of representative data are shown in Fig. 4. Both 0.78% Pt/Al_2O_3 and 0.24% Pt/SiO_2–Al_2O_3 exhibit a near zero-order dependence on toluene and a slight increase in the reaction order on H_2 as the temperature increases from 333 to 364 K. The slight deactivation mentioned previously can also be observed in Fig. 4, as a small reduction in

TABLE 1

Kinetics of Toluene Hydrogenation over Supported Pt at $P_{\mathrm{Tol}} = 50$ Torr and $P_{\mathrm{H_2}} = 685$ Torr

Catalyst (sample)	T_{red} (K)	H/Pt	$r_0 \times 10^{-7}$ [a]	E_A [b] $\left(\frac{\mathrm{kcal}}{\mathrm{mol}}\right)$	Activity at 333 K	
					μmol/s/g cat	TOF ($s^{-1} \times 10^3$)
0.96% Pt/SiO_2	723	0.96	0.68	10.3 ± 1.0	1.27	27
0.78% Pt/Al_2O_3 (I)	723	1.03	15.8	12.2 ± 2.1	1.48	37
0.78% Pt/Al_2O_3 (II)	723	1.03	200	14.2 ± 1.5	0.951	24
0.24% $Pt/SiO_2 \cdot Al_2O_3$ (I)	448	0.90	0.99	11.0 ± 1.1	0.578	52
0.24% $Pt/SiO_2 \cdot Al_2O_3$ (II)	448	0.90	1.29	11.2 ± 2.1	0.564	51
0.24% $Pt/SiO_2 \cdot Al_2O_3$	673	0.58	0.81	10.9 ± 2.1	0.590	82
0.24% $Pt/SiO_2 \cdot Al_2O_3$	723	0.44	0.99	11.0 ± 1.4	0.603	112
0.95% Pt/TiO_2 (LTR)	473	0.73	79.0	12.9 ± 1.7	2.77	78
0.95% Pt/TiO_2 (HTR)	773	0.021	39.2	14.4 ± 3.1	1.34	—
0.09% Pt/TiO_2 (LTR) (I)	473	0.80	5.18	13.9 ± 3.1	0.041	11
0.09% Pt/TiO_2 (LTR) (I)[c]	473	0.80	2.20	12.7 ± 1.9	0.099	27
0.09% Pt/TiO_2 (LTR) (II)	473	0.80	0.047	10.6 ± 4.2	0.052	14
0.09% Pt/TiO_2 (HTR)	773	nil	0.024	10.3 ± 2.8	0.042	—

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

[b] With 95% confidence limits.

[c] Catalyst rereduced between runs.

TABLE 2

Previous Results for Toluene Hydrogenation over Pt

Catalyst	Reaction conditions			E_A $\left(\frac{\mathrm{kcal}}{\mathrm{mol}}\right)$	Activity		TOF at 333 K ($s^{-1} \times 10^3$)	Ref.
	T (K)	$P_{\mathrm{H_2}}$ (Torr)	P_{Tol} (Torr)		mmol/s/g Pt	TOF ($s^{-1} \times 10^3$)		
6.3% Pt/SiO_2	298	755	5	—	—	10	62[a]	(*20*)
5% Pt/SiO_2	378	—	—	6.0	—	6800[b]	2310	(*21*)
5% Pt/Al_2O_3	378	—	—	6.0	—	7500[b]	2548	(*21*)
1% Pt/Al_2O_3	323	744	16	8.4–10.5	—	9	15	(*22*)
10% Pt/Glass	340	703	57	17.5	0.622	13	7	(*23*)
Pt/MgO(100)[c]	475	750	7	11.0	0.0002 –0.003	0.04–0.59[d]	—	(*24*)
Pt/α-$Al_2O_3(1\bar{1}02)$[c]	466	750	7	—	0.0007 –0.004	0.14–0.78[d]	—	(*24*)
α-$Al_2O_3(1\bar{1}02)$	466	750	7	—	0	—	—	(*24*)
1.68% Pt/NaY	373	—	—	12.0	—	—	—	(*25*)
Pt–Cu/NaY	373	—	—	16.0	—	—	—	(*25*)
Pd powder	413	680	50	10.8	0.0004	34	1	(*2*)
1.1% $Pd/SiO_2 \cdot Al_2O_3$ (red. at 448K)	413	680	50	12.2	0.645	204	6	(*2*)

[a] Calculated assuming $E_A = 10.3$ kcal/mol.

[b] Data acquired from pulse reactor.

[c] Catalyst prepared by implanting Pt on oxide surface.

[d] Assuming 100% Pt dispersion.

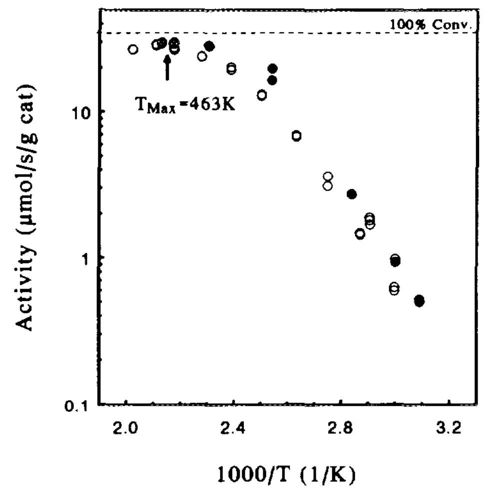

FIG. 2. Temperature effect on toluene hydrogenation over 0.78% Pt/Al_2O_3 at 50 Torr Tol and 685 Torr H_2. Open symbols represent an ascending-temperature sequence and filled symbols represent a descending-temperature sequence.

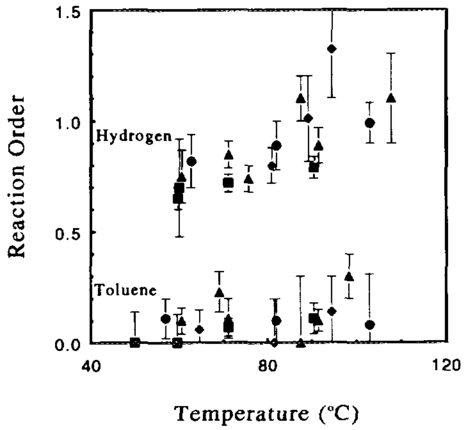

FIG. 3. Reaction orders for toluene hydrogenation over supported Pt: 0.78% Pt/Al_2O_3 (■), 0.96% Pt/SiO_2 (●), 0.09% Pt/TiO_2 (◆), and 0.24% $Pt/SiO_2 \cdot Al_2O_3$ (▲). The dependency on H_2 was measured at 50 Torr Tol and the dependency on toluene was measured at 685 Torr H_2. The error bars represent 95% confidence limits.

activity can be seen following a sequence of decreasing and increasing the H_2 or toluene partial pressure.

DISCUSSION

Based on LEED studies (*12*) and the out-of-plane C–H stretching band observed in EELS spectra (*13*), toluene is assumed to adsorb on Pt surfaces in a π-bonded mode like benzene. A stepped surface should not change this kind of π-interaction significantly, except that dissociative adsorption (reversible C–H bond breaking) appears more likely to occur on a Pt 6(111) × (111) surface than on a Pt(111) single crystal (*14*). Saturation coverages on Pt (Bz/Pt_s = 0.08–0.17) and the work function changes at this coverage are similar for both benzene and toluene (*12, 13*), although toluene is considered to adsorb more strongly than benzene (*13*). TPD studies have shown that most of the irreversibly adsorbed toluene dehydrogenates during desorption (*13–15*), thus possibly leaving behind carbonaceous resides on the surface, and an adsorbed $C_6H_5CH_2$ species was proposed by Tsai and Muetterties based on their TPD study of deuterated toluene on Pt(111) (*14*) and Pt(100) (*16*). No studies of deuterium–toluene exchange on a Pt surface have been found in the literature, but results for D_2 and *p*-xylene over Pt/Al_2O_3 and Pt/SiO_2 show that the H atoms on the ring usually exchange more readily with deuterium than those in the side group (*17*); however, over Pt films the side-chain exchange rate was higher than that for ring exchange (*18*). The C–H bond strength in the methyl side group (88 kcal/mol) is lower than that in the aromatic ring (111 kcal/mol for benzene) (*19*). Exchange rates were up to three orders of magnitude higher than the deuteration rate (*17, 18*).

Toluene hydrogenation has been studied much less often than benzene hydrogenation and the few investigations that have involved Pt catalysts are listed in Table 2 (*20–25*). Some results from our previous study of Pd catalysts are also included for comparison. The reversible maximum in activity shown in Fig. 2 has been commonly observed in benzene hydrogenation over Group VIII metals, and it occurs for toluene hydrogenation over Pd (*2*). It has been successfully explained by the temperature-de-

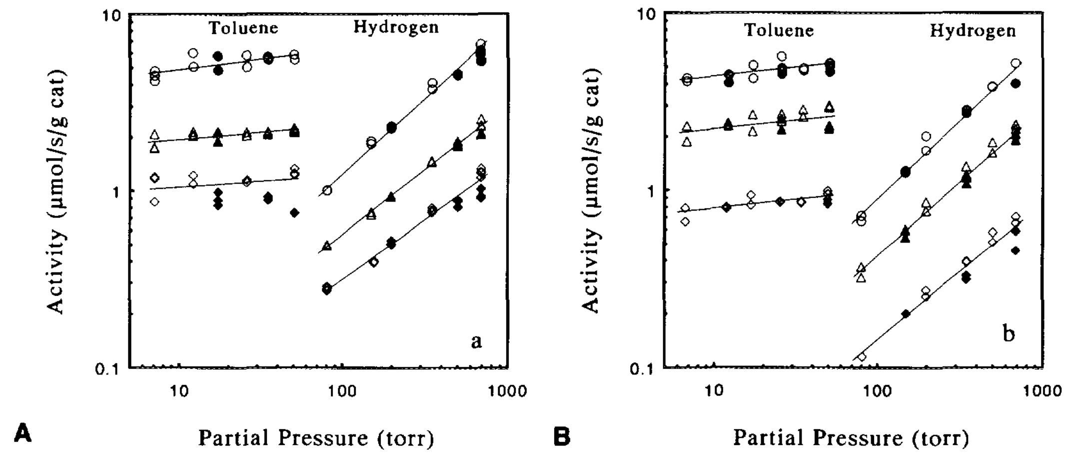

FIG. 4. Partial pressure dependencies for toluene hydrogenation over (a) 0.78% Pt/Al_2O_3 and (b) 0.24% $Pt/SiO_2 \cdot Al_2O_3$ at 333 K (◇, ◆), 344 K (△, ▲), and 364 K (○, ●). Open symbols represent a decreasing-pressure sequence and filled symbols represent an increasing-pressure sequence. The H_2 dependency was measured at 50 Torr Tol and the toluene dependency benzene was measured at 685 Torr H_2.

pendence of the surface coverages of the aromatic species based on a Langmuir–Hinshelwood mechanism (*26*); however, in Fig. 2 the conversion is approaching the equilibrium value and may also reflect the reverse reaction. Regardless, the maximum at 463 K for toluene hydrogenation is somewhat lower than that at 473 K for benzene hydrogenation over the same Pt/Al_2O_3 catalyst which could imply that the adsorption strength of toluene is slightly lower than that of benzene. The average activation energy of 12 ± 2 kcal/mol for toluene hydrogenation over these Pt catalysts is extremely similar to that for Pd catalysts (*2*), it is close to the activation energy for benzene hydrogenation on Pt (*4*), and it does not depend on the support. For a given support the TOF on Pt ranges from 8 to 80 times higher than that on Pd (*3, 5*). The specific activity of Pt is less dependent on the support than that of Pd, but this would be expected due to the higher TOFs on Pt which cause the relative contribution from the support to the overall activity to decrease. Regardless, $SiO_2 \cdot Al_2O_3$- and TiO_2-supported Pt have the highest activity, which is up to four times greater than that of Pt/SiO_2 and Pt/Al_2O_3. This pattern coincides with the findings for Pd catalysts (*2*). The similar trend in activity with respect to the type of support suggests that the model previously proposed for dispersed Pd may be applicable to dispersed Pt; that is, the metal–support interfacial region can provide additional activity by adsorbing toluene on acid sites on the oxide surface and allowing it to react with hydrogen via a spillover process (*1, 2, 27*).

Toluene adsorbs on oxides via a π-interaction with coordinatively unsaturated cations at the dehydroxylated surface or with acidic surface hydroxyl groups (*28–30*), and it has been assumed that this adsorption occurs with the ring parallel to the surface (*29*). BET monolayer coverages are similar to the saturation coverage on Pt, i.e., 1–2 molecule nm^{-2} (*29, 31*); however, application of the Kelvin equation indicates that pore condensation probably occurred under the conditions used in these previous adsorption studies, with the exception of one isotherm measured at 423 K by Talu *et al.* (*32*). If a surface area of 400 m^2/g is assumed for the silicalite they used, the surface coverage at 423 K was approximately 0.4 molecule nm^{-2}. Toluene adsorption on oxide surfaces is weaker than that on Pt surfaces because a prolonged evacuation at 300 K can remove almost all of the adsorbed toluene (*29*). However, heat of adsorption for toluene on an H-ZSM5 zeolite at 300 K has been reported to be about 15–20 kcal/mol (*31*, *33*), which is higher than its latent heat of condensation and indicates that toluene chemisorption can occur on acidic oxide surfaces. Although no hydrogenation is observed on oxides in the absence of a metal under our reaction conditions, D_2 exchange reactions proceed quite readily on numerous oxides (*34–38*). The mechanisms for these reactions are not well established, but it is known that activation energies are lower and that the ring H atoms are more easily exchanged than H atoms in the side groups. It has been proposed that the aromatic molecule adsorbs on a cation site (i.e., Al^{3+}) or on a hydroxyl group and exchanges via proton transfer with protons on the oxide surface (*35*). These studies show that toulene can adsorb on oxide surfaces under the reaction conditions used in this study, but that the exchange reaction proceeds independently of the hydrogenation reaction (*34–38*). Spilled-over hydrogen on SiO_2 and Al_2O_3 surfaces can hydrogenate benzene (*39–41*); consequently, it is expected that adsorbed toluene can also react with spilled-over hydrogen. As the concentration of hydrogen on the support surface is highest in the vicinity of the metal particles, the metal-support interfacial region could contribute to the overall activity if the concentration of adsorption sites for toluene is high enough and the hydrogen transport rate is sufficiently rapid.

Based on the model previously proposed, the overall activity can be separated into that from the metal surface and that from the interfacial region (*1–4*). If we presume that the Pt/SiO_2 and Pt/Al_2O_3 catalysts provide activity only from the Pt surface, then the relative contributions from the interfacial region for the Pt/TiO_2 (LTR) and $Pt/SiO_2 \cdot Al_2O_3$ samples can be estimated by subtracting the average TOF of the former two catalysts from the overall TOFs of the latter catalysts. This calculation indicates that up to 75% of the overall activity can be attributed to the interfacial region. This relative activity enhancement is significant, but it is lower than that obtained for benzene and toluene hydrogenation over Pd catalysts (*1*, *2*). Pure TiO_2 and $SiO_2 \cdot Al_2O_3$ without any metal were inactive for this reaction even though the same amount of Cl was present via HCl addition (*2*); consequently, some type of synergistic metal–support interaction, such as that proposed in these two earlier studies, must be invoked to explain the activity enhancement.

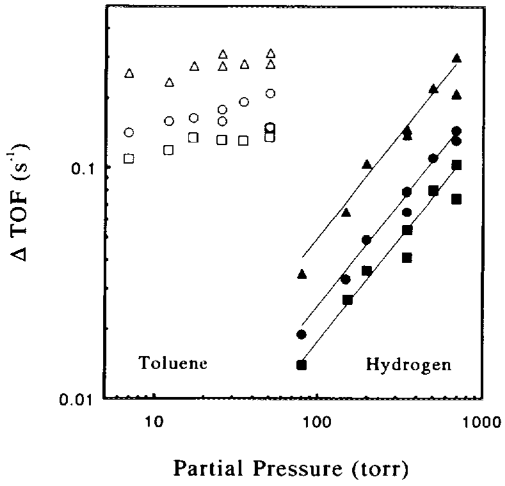

FIG. 5. Calculated activity contributions from the metal–support interfacial region during toluene hydrogenation at 333 K (□, ■), 344 K (○, ●), and 364 K (△, ▲).

In an effort to ascertain the kinetic behavior associated with the reaction in the interfacial region, the differences in TOFs between $Pt/SiO_2 \cdot Al_2O_3$ and Pt/Al_2O_3 were determined under similar partial pressure conditions from Fig. 4, and the results are shown in Fig. 5. The activity attributed to the interfacial region shows an essentially temperature-independent reaction order on H_2 of 0.9, which is close to the first-order dependence found for the comparable Pd catalysts (*2*). The difference in reactivity among different supports is expected to be related to the number of adsorption sites on the oxide surface and possibly to the strength of the interaction between the oxide and the toluene. Toluene can interact with acid sites on the oxide via the π-electron cloud, and an acid-catalyzed hydrogenation mechanism for benzene in the liquid phase has been discussed by Wristers (*42*); by analogy, a similar heterogeneous pathway on strong acid sites would be possible if activated hydrogen is available. This can qualitatively explain how a higher overall activity can be induced when Pt or Pd is dispersed on a more acidic support such as $SiO_2 \cdot Al_2O_3$. If this proposed reaction model is correct, acid strength and the acid site density should be key factors in high activity catalysts.

The consequences of the pretreatment of the more acidic catalysts such as Pt/TiO_2 and $Pt/SiO_2 \cdot Al_2O_3$ are not unambiguous. A high-temperature reduction (HTR) of Pt/TiO_2 causes the TiO_2 to migrate over the Pt surface and lower the activity (per gram metal) (*10, 11*). This occurs to a much lesser degree in the LTR samples because Pt dispersions are high. Although this blockage of the Pt surface after a HTR step causes a 35-fold reduction in adsorption capacity of the 0.95% Pt/TiO_2 catalyst, the activity decreases by only a factor of 2; consequently, one could infer that some of the activity is not directly associated with the exposed Pt surface. Similar behavior occurred for benzene hydrogeneration over these supported Pt catalysts (*3*), and the activity ratios between the HTR and LTR samples were similar in both reactions. It must be noted that Pt/TiO_2 catalysts after HTR must still be able to provide spilled-over hydrogen to the oxide surface, even though the Pt surface is almost completely covered by a TiO_x overlayer, as shown in Table 1 by the measurable activity of the 0.09% Pt/TiO_2 (HTR) sample despite its near-zero irreversible H_2 uptake. Regarding the $Pt/SiO_2 \cdot Al_2O_3$ samples, higher pretreatment temperatures decreased both the irreversible and the reversible hydrogen uptakes (*4*), but the activity per g Pt changed little. A similar decrease in chemisorption occurred with the series of $Pd/SiO_2 \cdot Al_2O_3$ catalysts (*2*), but in contrast, the activity of the latter samples also decreased with increasing reduction temperature. The reason for this difference is not presently known.

The addition of a methyl group to the aromatic ring has been found to decrease the catalytic activity over supported Pt, Pd, Rh, and Co (*2, 22, 23, 43, 44*). At identical reaction conditions of 50 Torr Bz or Tol and 685 Torr H_2, TOFs for Tol hydrogenation are comparable to or slightly higher than those for Bz hydrogenation, as shown in Table 3; however, when compared to Bz hydrogenation at 35 Torr, Tol TOFs are consistently lower and close to ratios previously reported for Pt (*22, 23*). At 50 Torr, toluene activity over Pd was 40–80% of the benzene activity (*1, 2*). Because both reactions are essentially zero order, this difference in activity is more likely due to a difference in the intrinsic rate constants rather than to surface coverage effects, especially since the competitive adsorption of toluene on Pt appears to be favored compared to benzene (*45*), although it is possible that the influence of H-deficient surface species is playing a role here.

The reaction order on hydrogen increases with temperature, while that of toluene remains almost constant (Fig. 3). The near zero-order dependence on toluene is consistent with the general understanding that the surface coverage of toluene is near saturation. The type of support does not seem to have a significant effect on the reaction orders, which suggests that the slow step for hydrogen addition to the ring may be similar for all these supported catalysts. This temperature dependence of the H_2 reaction order did not occur for benzene hydrogenation over these Pt catalysts (*3*), but it has been reported for both hydrogen and either benzene or toluene during hydrogena-

TABLE 3

Activity Comparison between Benzene and Toluene Hydrogenation over Pt Catalysts

Catalyst	TOF[a] ($s^{-1} \times 10^3$)		N_T/N_B	Rate on oxide sites[b]			
	Bz[b]	Tol		TOF normalized to Pt_s ($s^{-1} \times 10^3$)		Molecules s^{-1} $cm^{-2} \times 10^{-12}$	
				Bz	Tol	Bz	Tol
0.96% Pt/SiO_2	33 (72)	27	0.82 (0.38)	—	—	—	—
0.78% Pt/Al_2O_3	15 (36)	24	1.60 (0.67)	—	—	—	—
0.24% $Pt/SiO_2 \cdot Al_2O_3$ (723 K reduced)	72 (316)	112	1.56 (0.35)	48 (262)	87	0.039 (0.21)	0.071
0.95% Pt/TiO_2 (LTR)	78 (168)	78	1.00 (0.46)	54 (114)	53	2.4 (5.0)	2.3
0.95% Pt/TiO_2 (HTR)	51[c] (117)	38[c]	0.74 (0.32)	—	—	—	—

[a] Compared at $P_{Bz} = P_{Tol} = 50$ Torr, $P_{H_2} = 685$ Torr, and 333 K; numbers in parentheses represent benzene hydrogenation at $P_{Bz} = 35$ Torr, $P_{H_2} = 700$ Torr (from Ref. (*4*)).

[b] Calculated by (overall TOF) − (average TOF on Pt/SiO_2 and Pt/Al_2O_3).

[c] Based on dispersion of the LTR sample.

tion over a Ni/KY zeolite catalyst between 403 and 523 K (*46*). With Pd, a marked increase occurred in H_2 reaction order from 0.5 to nearly 4 as the temperature increased from 353 to 573 K, while a near-zero reaction order on benzene existed between 350 and 450 K but increased at higher temperature (*1*). These trends can be explained by a surface dehydrogenation reaction occurring concurrently with hydrogenation to form hydrogen-deficient species on the metal surface (*47*), and a reaction model invoking such a reaction sequence describes the data of both benzene and toluene hydrogenation well, as discussed in the following paper (*48*).

SUMMARY

The activation energy and the reaction orders on H_2 and toluene for toluene hydrogenation over Pt were independent of the support and of the catalyst pretreatment. The activation energy was 12 ± 2 kcal/mol and the reaction was near zero-order on toluene between 333 and 373 K; however, the reaction order on hydrogen increased from below 0.7 at 333 K to over unity at 373 K. The turnover frequency was affected by the support, varied by a factor of four, and followed the sequence $Pt/SiO_2 \cdot Al_2O_3 > Pt/TiO_2 > Pt/Al_2O_3 \cong Pt/SiO_2$. This trend is similar to that found previously with Pd catalysts, and the model previously proposed which attributed the enhanced activity to an additional reaction between toluene adsorbed on the oxide surface and the spilled-over hydrogen in the metal–support interfacial region is again applicable.

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