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The Effect of Metal-Support Interactions on the Hydrogenation of Benzaldehyde and Benzyl Alcohol

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Both rates (per g catalyst) and turnover frequencies for benzaldehyde hydrogenation were markedly enhanced on Pt/TiO_2 after a high-temperature reduction (HTR) step, compared to either Pt/TiO_2 after a low-temperature reduction (LTR) step, Pt/SiO_2 or Pt/Al_2O_3. All these catalysts consisted of dispersed 1-nm Pt crystallites and all gave similar activation energies of 8 ± 2 kcal/mole. More importantly, Pt/TiO_2 (HTR) retained a selectivity to benzyl alcohol of 100% up to conversions of 80%, whereas significant amounts of toluene and benzene began to be formed at conversions above 20% with the other Pt catalysts, including Pt powder. The specific activity for pure benzyl alcohol hydrogenation was similar to that for pure benzaldehyde on Pt/Al_2O_3 and Pt/TiO_2 (LTR), but it was greatly suppressed on Pt/TiO_2 (HTR). Thus, in addition to a higher formation rate of benzyl alcohol and less competitive benzyl alcohol adsorption compared to benzaldehyde, the lower intrinsic rate constant for benzyl alcohol hydrogenation further enhances the maintenance of high selectivity to benzyl alcohol at high conversions. A simple Langmuir–Hinshelwood model invoking the addition of the second H atom to benzaldehyde as the rate-determining step fit the data well. © 1997 Academic Press

INTRODUCTION

The choice of an appropriate support upon which to disperse a metal can have a significant effect on both the activity and selectivity in certain reactions, such as the hydrogenation of molecules containing carbonyl bonds (1, 2). Titania has proven to be especially good for this purpose, and increases in specific activities, such as turnover frequencies, have been obtained during hydrogenation of CO (3), acetone (4), crotonaldehyde (5), acetophenone (6), and phenyl-acetaldehyde (7, 8) over Pt/TiO_2 catalysts. Furthermore, in reactions with molecules containing both carbonyl and unsaturated C=C bonds, hydrogenation of the C=O group can be enhanced to increase the intramolecular selectivity to desired intermediate products, such as crotyl alcohol (5), 1-phenylethanol (6), and 2-phenylethanol (7, 8). To study this metal-support interaction (MSI) further and to examine the influence of the aromatic ring on reactivity of the carbonyl bond, benzaldehyde hydrogenation over these same Pt catalysts was also investigated, and the results are presented here.

EXPERIMENTAL

Except for Pt/SiO_2, the Pt catalysts were prepared by an incipient wetness technique using H_2PtCl_6 (Aldrich, 99.995%) dissolved in distilled, deionized water and η-Al_2O_3 (prepared by calcination of alumina β-trihydrate in air at 873 K, Exxon Research and Engineering Company, 245 m^2/gm), SiO_2–Al_2O_3 (Davison grade 979, 400 m^2/gm), and TiO_2 (Degussa P25, 50 m^2/gm) as support materials. Pt/SiO_2 was prepared by an ion-exchange method using $Pt(NH_3)_4Cl_2$ (Strem) as a precursor (9). All support materials were calcined 2 h at 773 K in air before impregnation, and the impregnated catalysts were dried at 393 K overnight before storage in a desiccator. Pt powder (Johnson Matthey, Puratronic, 99.999%) was mixed with precalcined SiO_2 powder, heated under O_2 at 673 K, and then treated with hydrogen prior to reaction.

One of these pretreatment procedures was followed with each catalyst:

Pretreatment A. Pt/SiO_2 and Pt/η-Al_2O_3 were treated under flowing He (50 cm^3 (STP)/min) at 393 K for 30 min, then under hydrogen at 533 K (50 cm^3 (STP)/min) for another 30 min before heating under hydrogen to 723 K and holding at that temperature for 1 h before evacuating at 673 K for 1 h or cooling under H_2.

Pretreatment B. Pt/TiO_2 (LTR) was treated under flowing He (50 cm^3 (STP)/min) at 423 K for 30 min, reduced under flowing hydrogen (50 cm^3 (STP)/min) at 473 K for 2 h before evacuating at that temperature for 1 h or cooling under hydrogen.

Pretreatment C. Pt/TiO_2 (HTR) was treated under flowing He (50 cm^3 (STP)/min) at 423 K for 30 min, heated under flowing hydrogen (50 cm^3 (STP)/min) to 533 K and held at this temperature for 30 min, then heated to 773 K and reduced at that temperature for 1 h before cooling to 723 K and evacuating for 1 h or cooling under H_2.

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Chemisorption was carried out at 300 K in a metal adsorption system giving a base pressure of 10^{-7} Torr at the sample and using a Texas Instruments pressure gauge (10). The H_2 (MG Ind., 99.999%) and CO (Matheson, 99.99%) were passed through a molecular sieve trap (Supelco) and an Oxytrap (Alltech Assoc). Both total and reversible uptakes on Pt were measured by consecutive isotherms with a 30-min evacuation in between and extrapolating each isotherm to zero pressure. A dispersion ($D = Pt_{surf}/Pt_{total}$) of unity corresponds to crystallites of about 1 nm or smaller.

Benzaldehyde (Aldrich, 99.98%) and benzyl alcohol (Aldrich, 99.98%) were degassed by several freeze-thaw cycles under a nitrogen purge and stored in a nitrogen-purged glove bag. H_2 and He (MG Ind., 99.999%) were passed through molecular sieve traps (Supelco) and Oxytraps (Alltech Assoc). A mixture of benzaldehyde (BNZALD) and H_2 or benzyl alcohol (BNZALC) and H_2 at atmospheric pressure and a total flow rate of 50 cm^3 (STP)/min was passed through a glass reactor containing 15–70 mg catalyst which was heated in a fluidized sand bath to reaction temperatures varying between 333 K and 493 K. To provide a wide range of conversion, space velocities were also varied. The effluent gas was analyzed by a gas chromatograph (H-P 5890 Series II) with a single TC detector and a 10-ft SP-2100 column. Arrhenius runs were conducted at BNZALD partial pressures of 3 Torr and 9 Torr and a hydrogen partial pressure near 740 Torr. The ascending temperature sequence was followed by a descending temperature run to detect any deactivation. The reactor effluent was passed through an ice/water trap downstream from the GC sampling valve. The stainless steel lines and the gas sampling valve were maintained at 423 K to assure no BNZALD condensation. Because this was a vapor-phase study conducted at atmospheric pressure, the possibility of pore condensation had to be considered. Pore size distributions determined from N_2 desorption measurements gave average pore diameters of 3, 5, 7, and 10 nm for η-Al_2O_3, SiO_2, SiO_2–Al_2O_3, and TiO_2, respectively. Using the Kelvin equation, it was calculated that operation above 333 K with 3 Torr BNZALD and above 353 K with 10 Torr BNZALD would avoid pore condensation (8). Liquid BNZALD or BNZALC was pumped into a preheated upstream section of the reactor using a Sage syringe pump and flashed to produce the desired partial pressure. Details of the system have been given previously (4–9). Because of the low flow rate required, nearly 90 min were needed for the partial pressure to stabilize under reaction conditions. Calculations indicated mass transfer limitations were absent or inconsequential.

RESULTS

Table 1 gives the H_2 uptakes measured on the fresh catalysts at 300 K. Pt was well dispersed in all the supported catalysts with dispersions of unity and crystallite sizes on the order of 1 nm. The unsupported Pt powder had a low surface area indicating a crystallite size of about 1 micron, in good agreement with BET measurements. Reduction of Pt/TiO_2 at 773 K decreased adsorption by an order of magnitude to a small uptake of 2.1 μmoles/g. CO chemisorption was also conducted on this sample (See Table 1) because CO can adsorb on single Pt atoms; thus the irreversible uptake may be higher than that obtained from dissociative hydrogen chemisorption. However, both values were low and similar, indicative of the SMSI state (11).

TABLE 1

Hydrogen Chemisorption on Pt Catalysts at 300 K

Catalyst	T_{red} (K)	H_2 uptake (μmoles/g cat) Reversible	Irreversible	Total	$\frac{H_{total}}{Pt_{total}}$	d (nm)
0.78% Pt/η-Al_2O_3	723	9.0	13.0	22.0	1.09	1.0
0.96% Pt/SiO_2	723	9.0	19.0	28.0	1.14	1.0
0.65% Pt/TiO_2 (LTR)	473	10.0	12.0	22.0	1.32	1.0
0.65% Pt/TiO_2 (HTR)	773	1.0	1.1	2.1	0.12	—
			5.0[a]		0.15[a]	—
0.24% Pt/SiO_2–Al_2O_3	448	4.0	3.0	7.0	1.15	1.0
Pt powder	723	1.4	1.7	3.1	0.0012	940

[a] Indicates CO chemisorption data.

Although the least favored thermodynamically, BNZALC was the primary hydrogenation product of BNZALD over all the Pt catalysts studied, with benzene and toluene typically increasing with higher conversions. Thermal response factors are available for benzene, toluene, cyclohexane, and methylcyclohexane (12), but the respective values of 109 ± 12 and 138 ± 16 for BNZALD and BNZALC had to be determined experimentally (8). Some deactivation was observed during BNZALD hydrogenation. To determine if this were due primarily to sintering or to poisoning by a carbonaceous overlayer, used Pt/Al_2O_3 and Pt/SiO_2 samples were regenerated by calcination in a 20% O_2, 80% He gas mixture at 673 K for 1 h. They were then re-reduced at 723 K for 1 h, evacuated, and H_2 isotherms were remeasured. Total uptakes were decreased by only 10% on each catalyst, thus eliminating sintering as an explanation of significant deactivation (8). This result is consistent with those of Rylander, who reported that both aliphatic and aromatic aldehydes deactivated Pt catalysts during liquid-phase BNZALD hydrogenation, but the catalysts could be regenerated by periodic treatments with oxygen (13).

The first measurement of activity could not be made until 90 min after introduction of the reactant because of the time required for the partial pressure to stabilize.

Subsequent activity measurements for BNZALD hydrogenation were sometimes complicated by deactivation of the Pt catalyst during the early period on stream. Most of the Arrhenius runs were usually conducted under approximately differential conditions by keeping conversions below 20%; however, at higher conversions the mass balance equation for an integral reactor was used along with the appropriate rate expressions to obtain rate constants which were used to determine E_a values. Representative plots obtained after the initial deactivation had occurred and relatively stable behavior was attained are shown in Fig. 1. The rates and TOFs (molecules/s/Pt_{surf}) for hydrogenation of BNZALD at 353 K and an aldehyde pressure of 3 Torr are listed in Table 2. The apparent activation energies varied from 5.0 to 10.2 kcal/mole and the TOFs ranged from 8 to 680 s^{-1}. An Arrhenius run was also conducted with 0.24% $Pt/SiO_2–Al_2O_3$ (pretreatment B with a reduction temperature of 448 K) to examine the effect of surface acidity on BNZALD hydrogenation. These results showed no BNZALC yield and no vapor-phase products at low temperature, and only benzene, a hydrogenolysis product, was detected at higher temperatures; thus the rate, apparent activation energy, and TOF for benzene production is reported for this catalyst in Table 2. The pure oxide supports were found to be inactive for BNZALD hydrogenation. A minimum TOF for Pt/TiO_2 (HTR) was obtained by normalizing the rate to the number of surface Pt atoms measured in the Pt/TiO_2 (LTR) sample, and these values are listed in brackets. The activities for some of the Pt catalysts were also determined at a BNZALD partial pressure of 9 Torr and these values are reported in Table 3. At conversions above 20% rate constants were again determined using the rate expression for an integral reactor. Plotting these k values versus reciprocal temperature gave apparent activation energies varying from 4 to 14 kcal/mole, and the TOFs for the Pt/TiO_2 (HTR) catalysts were again much higher than the corresponding values for Pt/SiO_2 and $Pt/\eta-Al_2O_3$, which were higher than the values reported for the same catalysts at a BNZALD pressure of 3 Torr. Partial pressure dependencies were determined at 355 K immediately after the Arrhenius run. The BNZALD partial pressure was held at 3 Torr while the H_2 partial pressure was varied; then the H_2 partial pressure was held near 740 Torr while the BNZALD partial pressure was varied. The results are shown in Fig. 4 while the reaction orders are listed in Table 4. The reaction orders on BNZALD were zero for Pt/TiO_2 (LTR) and Pt/TiO_2 (HTR), 0.10 for Pt powder, and increased slightly

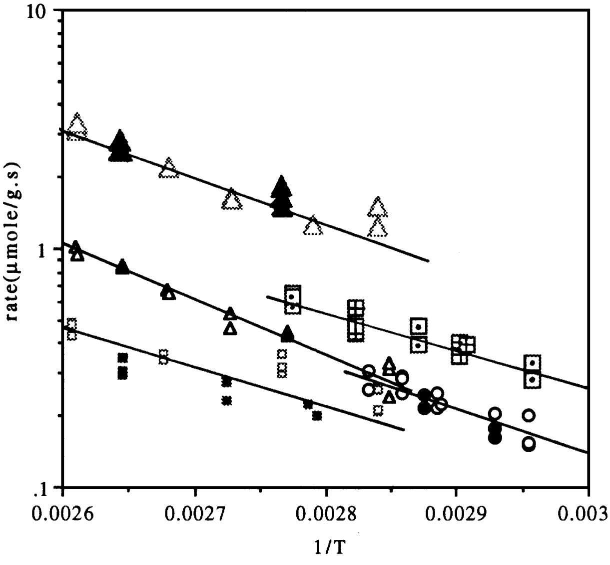


FIG. 1. Arrhenius plots for benzaldehyde hydrogenation; $P_{BNZALD} = 3$ Torr, $P_{H_2} = 740$ Torr: (△), Pt/TiO_2 (HTR); (△), Pt/TiO_2 (LTR); (□), Pt/SiO_2; (○), $Pt/\eta-Al_2O_3$; (□), Pt powder. Ascending—open symbols; descending—filled symbols.

TABLE 2

Steady-State Turnover Frequencies for Benzaldehyde Hydrogenation on Pt Catalysts at 353 K

Catalyst	T_r (K)	$Rate_{BNZALD}$ (µmole/ s · g cat)	E^a (kcal/ mole)	TOF^b ($s^{-1} \times 10^3$)	Conv. (%)
0.78% $Pt/\eta-Al_2O_3$	723	0.31	9.7 ± 1.2	7.7	8–18
0.96% Pt/SiO_2	723	0.50	7.2 ± 0.8	10.1	11–20
0.65% Pt/TiO_2 (LTR)	473	0.28	10.2 ± 0.5	8.4	2–16
0.65% Pt/TiO_2 (HTR)	773	1.50	5.8 ± 1.6	360 (45)	12–24
0.65% Pt/TiO_2 (HTR)	773	2.84	7.1 ± 0.6	680 (85)	10–20
0.65% Pt/TiO_2 (HTR)	773	1.37	8.2 ± 0.7	330 (41)	3–6
0.65% Pt/TiO_2 (HTR)	773	0.90	6.0 ± 1.5	210 (27)	40–80
Pt powder	723	0.23	5.0 ± 0.9	38.0	8–17
0.24% $Pt/SiO_2–Al_2O_3$	448	0.003^c	13.2^c ± 1.8	0.24^c	2–9^c
TiO_2	473	0	—	0	0
TiO_2	723	0	—	0	0
$SiO_2–Al_2O_3$	448	0	—	0	0

Note. $P_{BNZALD} = 3$ Torr, $P_{H_2} = 750$ Torr.

[a] With 95% confidence limits.

[b] TOF in parentheses based on dispersion of unity for LTR sample.

[c] Benzene formation.

TABLE 3

Steady-State Turnover Frequencies for Benzaldehyde Hydrogenation on Pt Catalysts at 353 K

Catalyst	T_r (K)	$Rate_{BNZALD}$ (µmole/ s · g cat)	E^a (kcal/ mole)	TOF^b ($s^{-1} \times 10^3$)	Conv. (%)
0.78% $Pt/\eta-Al_2O_3$	723	0.58	3.6 ± 1.0	14	20–35
0.78% $Pt/\eta-Al_2O_3$	723	0.58	5.2 ± 0.8	14	20–40
0.96% Pt/SiO_2	723	1.18	14.0 ± 1.5	24	6–18
0.65% Pt/TiO_2 (HTR)	773	2.3	4.8 ± 0.4	550 (69)	50–80
0.65% Pt/TiO_2 (HTR)	773	1.8	8.0 ± 0.7	430 (54)	2–5

Note. $P_{BNZALD} = 9$ Torr, $P_{H_2} = 740$ Torr.

[a] With 95% confidence limits.

[b] TOF reported in parentheses based on chemisorption on LTR sample.

TABLE 4

Partial Pressure Dependencies[a]

(a) Benzaldehyde Hydrogenation at 355 K $\left(\text{rate} = kP^{a}_{\text{BNZALD}}P^{b}_{H_2}\right)$

Catalyst	a	b
0.65% Pt/TiO_2 (LTR)	0.0 ± 0.09	0.59 ± 0.05
0.65% Pt/TiO_2 (HTR)	0.0 ± 0.12	0.78 ± 0.11
Pt powder	0.16 ± 0.04	0.99 ± 0.18
0.96% Pt/SiO_2	0.18 ± 0.03	0.81 ± 0.08
0.78 $Pt/\eta\text{-}Al_2O_3$	0.30 ± 0.07	0.52 ± 0.11

(b) Benzyl Alcohol Hydrogenation at 393 K $\left(\text{rate} = kP^{c}_{\text{BNZALC}}P^{d}_{H2}\right)$

Catalyst	c	d
0.65% Pt/TiO_2 (LTR)	0.0	0.6
0.65% Pt/TiO_2 (HTR)	0.1	0.5

[a] With 95% confidence limits.

to values of 0.18 and 0.31 for Pt/SiO_2 and $Pt/\eta\text{-}Al_2O_3$, respectively. The hydrogen reaction orders varied from half to first order.

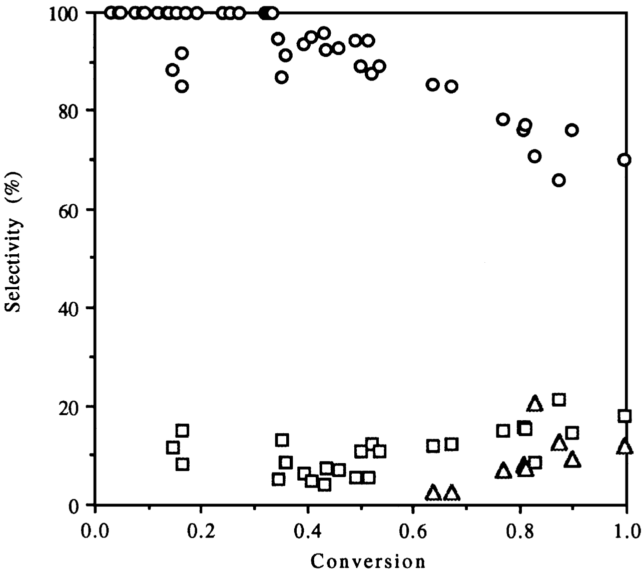


FIG. 2. Selectivity vs conversion for benzaldehyde hydrogenation over 0.78% $Pt/\eta\text{-}Al_2O_3$; $P_{\text{BNZALD}} = 3$ Torr, $P_{H_2} = 740$ Torr, and $T = 319$–450 K: (○), benzyl alcohol; (□), benzene; (△), toluene.

Any deactivation during the initial 90 min on stream could not be estimated because of the changing BNZALD partial pressure in the catalyst bed as it approached steady state, but rates could be measured accurately once the partial pressure stabilized. The steady-state activities in Tables 2 and 3 were measured after catalyst performance had stabilized and did not vary significantly with time. Table 5 compares the "early" activity and TOF, defined as that first measured after 90 min on stream, to the stabilized value obtained after longer times on stream when little additional deactivation was occurring. This comparison shows that the Pt/TiO_2 (HTR) catalysts were still the most active and showed a low level of deactivation while $Pt/\eta\text{-}Al_2O_3$ and Pt/TiO_2 (LTR) had suffered significant deactivation. The activity of Pt powder and Pt/SiO_2 appeared to have stabilized during the initial 90 min on stream as little further change in activity was observed.

Figures 2 and 3 show plots of selectivity versus conversion for $Pt/\eta\text{-}Al_2O_3$, Pt/TiO_2 (LTR), and Pt/TiO_2 (HTR) at a BNZALD pressure of 3 Torr. BNZALC was the main product formed over all the Pt catalysts except for $Pt/SiO_2{-}Al_2O_3$, in which case benzene was the only vapor-phase product detected. The selectivity can depend on both

TABLE 5

Comparison of "Early" Activity with Stabilized Activity

Catalyst	"Early"[a] activity (μmole/s · g)	Stabilized activity (μmole/s · g)	"Early"[a] TOF (s^{-1})	Stabilized TOF (s^{-1})
0.78% $Pt/\eta\text{-}Al_2O_3$	0.90	0.31	22	7.7
0.96% Pt/SiO_2	0.47	0.50	9.5	10.1
0.65% Pt/TiO_2 (LTR)	1.24	0.28	37	8.4
Pt powder	0.26	0.23	41	38
0.65% Pt/TiO_2 (HTR)	3.84	2.84	914 (114)[b]	680 (85)[b]
0.65% Pt/TiO_2 (HTR)	1.9	1.37	450 (57)[b]	330 (41)[b]

Note. $P_{\text{BNZALD}} = 3$ Torr, $P_{\text{total}} = 740$ Torr, $T = 353$ K.

[a] After 90 min on stream to allow BNZALD partial pressure stabilization.

[b] TOF in brackets based on dispersion of unity for LTR sample.

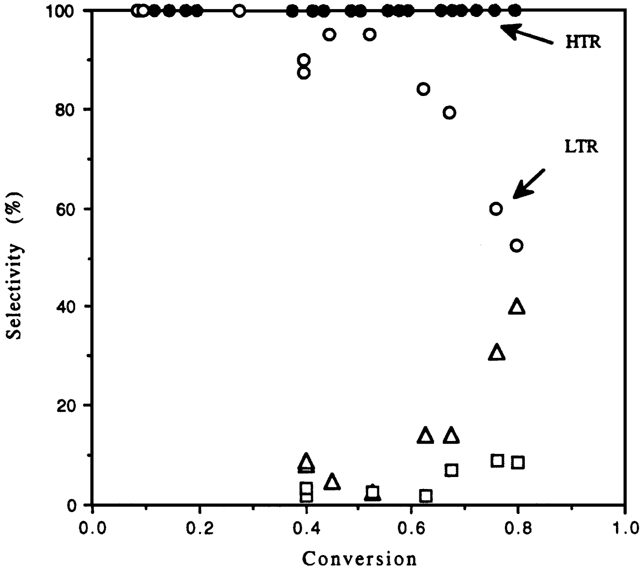


FIG. 3. Selectivity vs conversion for benzaldehyde hydrogenation over 0.65% Pt/TiO_2 (HTR) and 0.65% Pt/TiO_2 (LTR); $P_{\text{BNZALD}} = 3$ Torr, $P_{H_2} = 740$ Torr, and $T = 353$–450 K: (●), BNZALC (HTR); (○), BNZALC (LTR); (△), toluene (LTR); (□), benzene (LTR).

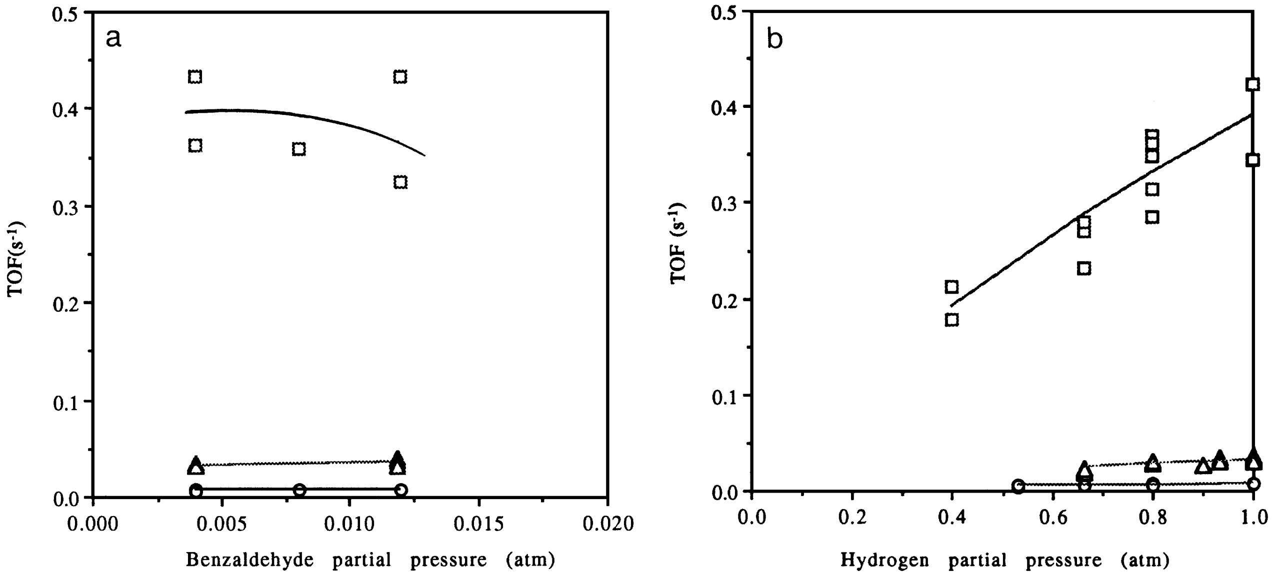


FIG. 4. Partial pressure dependencies on (a) BNZALD and (b) H_2 for benzaldehyde hydrogenation at 355 K over Pt catalysts: (○), Pt/SiO_2; (□), Pt/TiO_2 (HTR); (△), Pt powder.

conversion and temperature, and conversion was varied by changing either the space velocity or the temperature. BNZALC was always the only product at low conversions as reaction temperatures ranged from 353 K to 453 K. In general, the benzene hydrogenolysis product was usually observed as conversions increased and temperatures rose above 373 K, while toluene was formed at conversions greater than 50% and at temperatures near 423 K or higher.

The Pt/SiO_2–Al_2O_3 catalyst was obviously different because no BNZALC was ever detected by gas chromatography, even after 12 h on stream, and benzene became detectable only at higher temperatures. Inside the reactor after the run, a green waxy condensate was found which was dissolved in acetone and analyzed by fast atom bombardment with a Kratos MS 50 mass spectrometer in the Mass Spectroscopy Laboratory on campus (8). The high masses and peak positions suggested a long-chain polymer with a monomer unit of 90 amu, consistent with the formation of polymeric benzyl benzyls.

The hydrogenation of BNZALD over Pt/η-Al_2O_3 yielded BNZALC along with benzene and toluene at higher conversions. Benzene production was always higher than that of toluene, and the formation of either product was suppressed at lower conversion and lower temperature. A selectivity versus conversion plot for Pt/η-Al_2O_3 at 9 Torr BNZALD gave similar selectivity to BNZALC; for example, the product consisted of 80 mol% BNZALC at conversions near 70%, but toluene formation was higher than that of benzene in this case (8). Selectivity versus conversion plots for Pt/TiO_2 subjected to either an LTR or an HTR pretreatment are compared in Fig. 3. Pt/TiO_2 (HTR) showed 100% selectivity to BNZALC even at conversions near 80%. BNZALC was the main product formed over Pt/TiO_2 (LTR) at lower conversions, but large amounts of toluene were formed at higher conversions (40% selectivity to toluene at 80% conversion). Small amounts of benzene were formed over the LTR sample at conversions of 40% and above.

Only toluene and BNZALD were detected as products when BNZALC was hydrogenated over Pt/η-Al_2O_3 under differential conditions. Trace amounts of BNZALD were observed in the outlet stream when BNZALC and hydrogen were passed through an empty reactor, thus BNZALD peak areas in the chromatograms taken during BNZALC hydrogenation over Pt/η-Al_2O_3 were corrected for this background conversion. Figure 5 shows Arrhenius plots for BNZALC hydrogenation to toluene over Pt/TiO_2 (LTR), Pt/TiO_2 (HTR), and Pt/η-Al_2O_3, and it is apparent that deactivation occurs during this reaction over Pt/η-Al_2O_3. The figure shows that a 35% loss in activity at 413 K occurred during the descending and ascending Arrhenius runs; thus, the apparent activation energy varied from 4 to 12 kcal/mole, with an average value of 8 kcal/mole. Table 6 compares the activities and the apparent activation energies for BNZALC and BNZALD hydrogenation over Pt/η-Al_2O_3, Pt/TiO_2 (HTR) and Pt/TiO_2 (LTR). The average TOF for BNZALC hydrogenation over Pt/TiO_2 (HTR) is 30 times lower than the corresponding value for BNZALD hydrogenation, whereas the TOF values for both reactions on the other two catalysts are comparable, with that for the former reaction actually being higher on Pt/η-Al_2O_3. Table 4 also reports the partial pressure dependencies for BNZALC hydrogenation at 393 K on titania-supported Pt derived from the results in Fig. 6.

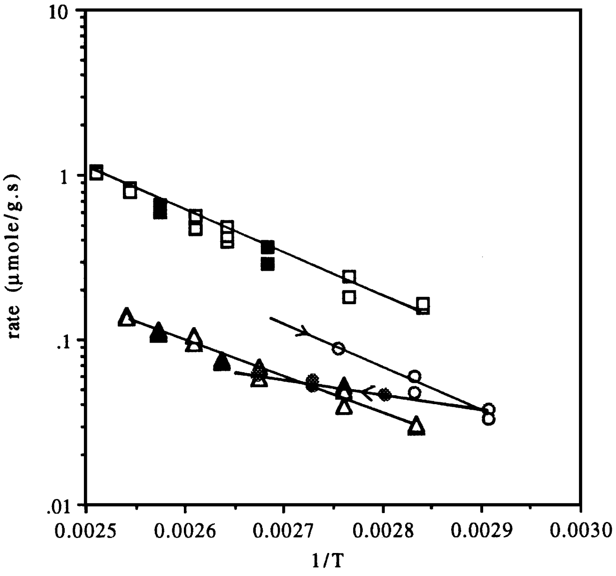


FIG. 5. Arrhenius plots for benzyl alcohol hydrogenation to toluene, $P_{BNZALC} = 3$ Torr: (□), Pt/TiO$_2$ (LTR); (△), Pt/TiO$_2$ (HTR); (○), Pt/η-Al$_2$O$_3$. Ascending—open symbols; descending—closed symbols.

TABLE 6

Turnover Frequencies for Benzaldehyde and Benzyl Alcohol Hydrogenation

Compound	Catalyst	E (kcal/ mole)	Rate (μmole/ s · g)	TOF[a] (s^{-1} × 10^3)
(1) BNZALC	0.78% Pt/η-Al$_2$O$_3$	8.0	0.44	11
	0.65% Pt/TiO$_2$ (LTR)	11.4	0.16	4.8
	0.65% Pt/TiO$_2$ (HTR)	7.1	0.074	17.5 (2.2)
	0.65% Pt/TiO$_2$ (HTR)	10.1	0.031	7.4 (0.9)
(2) BNZALD	0.78% Pt/η-Al$_2$O$_3$	9.7	0.31	7.7
	0.65% Pt/TiO$_2$ (LTR)	10.2	0.28	8.4
	0.65% Pt/TiO$_2$ (HTR)	6.9[b]	1.65[b]	395 (49)[b]

Note. $T = 353$ K, P (compound) = 3 Torr, $P_{H_2} = 740$ Torr.

[a] TOF reported in parentheses based on dispersion of LTR sample (100%).

[b] Average values from Table 2.

DISCUSSION

Until recently studies of BNZALD hydrogenation typically had been carried in the liquid phase using a solvent (13–25), and in addition, none of these early investigations had provided any specific activities for product formation. Southwick and Coven did compare BNZALD hydrogenation at room temperature and atmospheric pressure over Pd, Pt, Rh, and Ru dispersed on carbon and found Pd to be most active (14), while Adkins and Billica reported that Raney Ni catalysts gave a higher rate of hydrogenation that Pt and Pd catalysts and that BNZALC was always the primary product (15). In liquid-phase reactions the solvent can have a significant influence on activity and selectivity; for example, the rate of BNZALD hydrogenation over platinum oxide in various solvents decreased in the order acetone > acetic acid > ethyl acetate > petroleum ether > ethyl ether > pyridine > benzene (16). In another

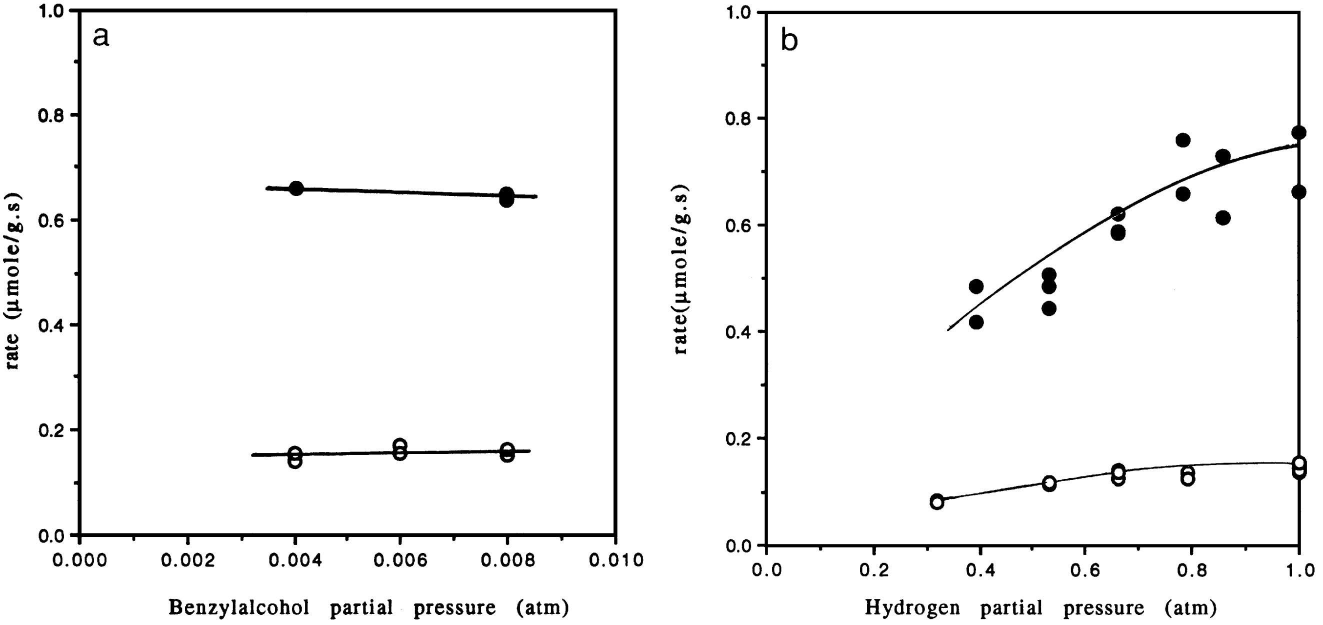


FIG. 6. Partial pressure dependencies for benzyl alcohol hydrogenation to toluene at 393 K: (a) BNZALC, (b) H$_2$: (●), Pt/TiO$_2$ (LTR); (○), Pt/TiO$_2$ (HTR).

comparison, the rate over 5% Pd/C decreased with solvent in the following order: acetic acid > methanol > ethylacetate > hexane > dimethylformamide > benzene > water (13). The rate of BNZALD reduction in most solvents typically declined after the reaction of one equivalent of hydrogen; therefore, high yields of BNZALC could be obtained by stopping the reaction at this point. The hydrogenation of BNZALD in methanol over platinum oxide was complicated by acetal formation; however, no acetal formation occurred when ethanol was used as a solvent (16). Meschke and Hartung found that the rate of toluene formation from BNZALC rapidly declined over Pd/C as the reaction progressed and that the reaction was further inhibited by the addition of toluene; however, toluene did not have any effect on the hydrogenation of BNZALD to BNZALC over Pd/C (17). They also showed that the rate of reduction of BNZALD to BNZALC in ethanol with Pd/C was zero order with respect to BNZALC. Comparable rates for BNZALD and BNZALC hydrogenation over Pd/C in acidified methanol were reported by Baltzly (18).

The presence of additives (promoters or poisons) can also affect this reaction. Carothers and Adams examined the effect of numerous transition metal compounds on the rate of BNZALD hydrogenation, and they found that small amounts of iron salts enhanced catalytic activity while Ti oxide and Al oxide had little or no effect on the reaction rate when mixed with platinic oxide (19). These authors speculated that the function of the iron salt or other promoters might be merely to eliminate or diminish any side reactions of BNZALD which created catalytic poisons. The same authors also found that bases like sodium, potassium, barium, and calcium hydroxides accelerated the reaction while hydrochloric, sulfuric, and nitric acids had no effect on the reaction rate; however, irrespective of the additives used, BNZALC was the exclusive first product formed and hydrocarbons were formed only after the reaction of more than one equivalent of hydrogen (19).

Nightingale and Radford found that hydrogenation of *o*-, *m*-, and *p*-hydroxybenzaldehydes over Cu chromite catalysts, typically at 220–240 atm and 373–403 K, gave the corresponding hydroxybenzylalcohols and cresols while *o*- and *p*-methoxybenzaldehyde gave the corresponding methoxybenzylalcohols (20). The same investigators reported that acetophenone hydrogenated at 338–358 K and 200 atm over Raney Ni yielded a product containing 75% ethyl benzene and variable amounts of aromatic carbinols whereas methylphenyl carbinol was the primary product over copper chromite catalysts; however, at 453–473 K and pressures of 300–340 atm, ethylbenzene was the only product formed over copper chromite (20). Jenck and Germain hydrogenated various aldehydes, ketones, and olefins over a copper chromite catalyst and found that, in general, aldehydes were more reactive than ketones, which in turn were more reactive than olefins, and a phenyl substituent was found to activate both C=C and C=O bond hydrogenation (21).

One recently published paper has reported that over Ru at 303 K some initial hydrogenation of the aromatic ring occurs to give a BNZALC/cyclohexane carbaldehyde ratio near 5 in either hexane or 2-propanol (26). Moulijn and coworkers have just provided liquid-phase hydrogenation rates of 0.15 to 5.7×10^{-2} mole/min $\cdot$ g at 420 K and 15 atm H_2 for pure BNZALD over Ni monolith catalysts (27). Lin *et al.* studied acetophenone hydrogenation over Pt catalysts and determined that phenylethanol was the primary product over Pt/SiO_2 and $Pt/\eta\text{-}Al_2O_3$, constituting 60–70% of the product stream at conversions near 50%, whereas Pt/TiO_2 reduced at high temperatures increased the selectivity to 90% or higher (6). This again demonstrated the ability of Pt/TiO_2 (HTR) to favor C=O bond hydrogenation, consistent with previous work (1); in contrast, TOFs for hydrogenation of aromatic molecules (9, 28–30) and unsaturated C=C bonds (2, 11) have remained essentially unchanged over the same catalyst. A model has been proposed invoking special sites formed at the platinum-titania interface which activate C=O bond hydrogenation (1); whereas hydrogenation of C=C bonds or the aromatic ring is typically a structure insensitive reaction that requires only Pt sites.

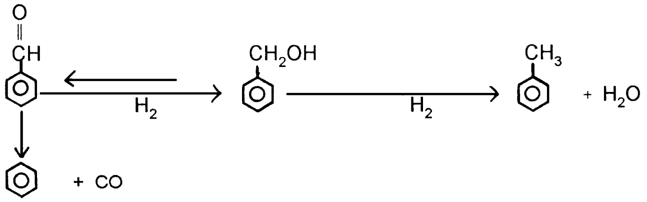
Finally, Rylander has reported that both aliphatic and aromatic aldehydes deactivate Pt catalysts (13), and Carothers and Adams found that BNZALD hydrogenation over Pt did not go to completion and the catalyst had to be reactivated with oxygen several times (19). Deactivation with Ni catalysts has also been mentioned (24). The Pt catalysts in this study also lost some of their initial activity before their performance stabilized, but they could be fully regenerated by a calcination step in oxygen at 673 K followed by reduction as they did not sinter. Similar deactivation and regeneration with oxygen has been reported during BNZALD hydrogenation over Pd and Ni (19).

In this investigation, the apparent activation energy for BNZALD hydrogenation on Pt catalysts fell between 5 and 10 kcal/mole at 3 Torr BNZALD while a somewhat wider range existed at 9 Torr. These values are similar to that reported for BNZALD hydrogenation on Ni (13 kcal/mole) (25), to those (3–9 kcal/mole) for acetophenone hydrogenation under similar reaction conditions (6, 31), and to the low values obtained for hydrogenation of crotonaldehyde on Pt (5) and acetophenone on copper chromite (32). Application of the Weisz criterion (33) gave very low values indicating insignificant diffusional resistance (8). BNZALC was the only product formed at low conversions, ca 20% or less. The comparison of TOFs in Table 2 clearly shows that Pt/TiO_2 (HTR) is more active than any other Pt catalyst, even if the minimum values are used, and the high rates also reflect this. The HTR pretreatment with Pt/TiO_2 increases rates and TOF values up to an order of magnitude compared to the LTR pretreatment, and the TOFs for all the Pt catalysts varied over two orders of magnitude, i.e., from 3.8 to 680 s^{-1} when based on sites capable of adsorbing hydrogen. TOF values for Pt and Ni can now be compared by using the appropriate activation energy from Table 2 and rate expression from Table 4 and calculating rates at the conditions used by Moulijn and coworkers (27). Assuming the most active Ni catalyst had the highest Ni loading, a TOF of 8.7 s^{-1} for Ni at 420 K and 15 atm H_2 is obtained; this compares to TOF values of 0.5 s^{-1} for Pt/SiO_2 and 29 (3.6) s^{-1} for Pt/TiO_2 (HTR). Similar increases in TOF with Pt/TiO_2 (HTR) were also obtained for acetophenone hydrogenation (6), and Coq *et al.* found that TiO_2-supported Ru (HTR) gave a high TOF for liquid-phase cinnamaldehyde hydrogenation at 333 K as well (34). Titania by itself is inactive for BNZALD hydrogenation.

As in previous studies, the enhanced specific activity with Pt/TiO_2 (HTR) is attributed to the creation of special sites at the platinum–titania interface, which presumably interact with the oxygen end of the carbonyl bond to polarize it and enhance its reactivity with hydrogen (1). However, it is important to emphasize that the large variation in steady-state TOF values in Table 2 can also reflect the effect of deactivation processes as well as intrinsic kinetic differences. To illustrate this, a comparison of early activities in Table 5 with those obtained under steady-state conditions shows that $Pt/\eta\text{-}Al_2O_3$ and Pt/TiO_2 (LTR) deactivate much more than Pt/SiO_2 and Pt powder, the latter of which remain within 10% of their early activity at steady state, while the Pt/TiO_2 (HTR) catalysts exhibit an intermediate degree of deactivation. Unfortunately, under our reaction conditions, the extent of deactivation during the first 90 min on stream cannot be determined.

Perhaps more important than the higher activity obtained with the Pt/TiO_2 (HTR) catalysts is the retention of high selectivity to BNZALC at high conversions, as demonstrated in Figs. 2 and 3. The marked influence of the pretreatment is clear in Fig. 3, and 100% BNZALC is obtained even at conversions of 80%. The retention of this high selectivity is obviously facilitated by the enhanced rate of formation of BNZALC over Pt/TiO_2 (HTR), but the inhibition of secondary reactions, such as BNZALC hydrogenation to toluene, is also necessary and must be a consequence of an alteration in competitive adsorption which prevents the readsorption of BNZALC. The results imply that adsorption of BNZALD on Pt is highly favored over BNZALC until product partial pressures become high enough to induce competitive adsorption, and this transition is markedly suppressed with Pt/TiO_2 (HTR) compared to Pt/TiO_2 (LTR) and typical Pt catalysts. The zero or near-zero order partial pressure dependencies on BNZALD in Table 4, indicative of high surface coverages, are consistent with this proposal, and the high TOFs in Table 6 for BNZALC hydrogenation in the absence of BNZALD also support this perspective. Apparent activation energies for BNZALC are again low, as expected. However, it is important to note that the TOF for BNZALC hydrogenation on Pt/TiO_2 (HTR) is actually decreased significantly compared to that for BNZALD, whereas the two TOF values are quite similar for $Pt/\eta\text{-}Al_2O_3$ and Pt/TiO_2 (LTR). This alteration obviously provides an additional factor to favor BNZALC selectivity. Such a reduction in the rate of hydrogenation of a reactive organic intermediate has not been observed in any of our previous studies (5, 7, 35), and an unequivocal explanation for this behavior cannot be offered at this time, but it is possible that the water produced during BNZALC hydrogenation may alter the catalyst.

Benzene formation was routinely observed at lower conversions, whereas toluene formation typically did not occur until higher conversions (and temperatures) were achieved, but the rate of benzene production remained low over the supported Pt catalysts and did not change significantly with conversion (or temperature). The TOFs for benzene and toluene hydrogenation are at least one order of magnitude higher than those for BNZALC and BNZALD; regardless, no cyclohexane or methylcyclohexane was detected in the product stream from any of the catalysts. This is undoubtedly due to the inhibition of benzene and toluene adsorption when these other compounds are present at high concentrations. The reasons why no initial ring hydrogenation occurs to form hexahydrobenzaldehyde are not clear, but they could be due to either the orientation of the BNZALD adsorbed on the catalyst surface or an electronic effect on the aromatic ring caused by the carbonyl group attached to it. During the BNZALC hydrogenation runs, a small amount of BNZALD was the only product detected other than toluene. Consequently, benzene formation appears to come only from the hydrogenolysis of BNZALD, and the reaction network for BNZALD hydrogenation under our reaction conditions can be simplified to the following sequence:



After changing to a GC column capable of separating CO and CH_4 from H_2, CO formation along with benzene was verified; no CH_4 was detected.

BNZALC is also the primary product during the liquid-phase hydrogenation of BNZALD over Pt catalysts (16, 23), and toluene formation was reported when acidic solvents were used. In our study, the use of an acidic support such as SiO_2–Al_2O_3 brought no beneficial change in the product distribution as no BNZALC was ever detected and only benzene formation at higher temperatures was observed. This latter reaction indicated that the Pt was not completely deactivated. BNZALD did not show any reactivity or retention on pure SiO_2–Al_2O_3. To clarify this behavior, H_2 and BNZALC were flowed over Pt/SiO_2–Al_2O_3 and neither unreacted BNZALC nor any product was observed in the effluent stream for many hours although traces of toluene were detected after 12 h on stream. The green waxy compound that had condensed inside the reactor was analyzed by mass spectroscopy and was found to be composed of a polymeric material with a monomer unit of 90 amu. Thus an acid-catalyzed polymerization reaction to form benzyl benzyls had occurred (36).

As indicated in Table 4, the partial pressure dependence on BNZALD was zero or near-zero while that for hydrogen fell between half and first order. A zero-order dependence on BNZALD has been reported for Ni (25). Various reaction models to describe BNZALD hydrogenation were examined and, although some could be eliminated (8), a number provided rate expressions consistent with the data shown in Fig. 4. The simplest of these is a straightforward Langmuir–Hinshelwood sequence with competitive adsorption and the addition of the second H atom as the rate determining step (rds), as shown below, where $*$ represents an active site:

$$H_2 + 2* \overset{K_{H_2}}{\rightleftharpoons} 2H* \qquad [1a]$$

$$C_6H_5CHO + * \overset{K_{BNZALD}}{\rightleftharpoons} C_6H_5CHO* \qquad [1b]$$

$$C_6H_5CHO* + H* \overset{K_1}{\rightleftharpoons} C_6H_5CH_2O* + * \qquad [1c]$$

$$C_6H_5CH_2O* + H* \xrightarrow{k} C_6H_5CH_2OH* + * \qquad [1d]$$

$$C_6H_5CH_2OH* \overset{K_2}{\rightleftharpoons} C_6H_5CH_2OH + * \qquad [1e]$$

Assuming only H atoms and BNZALD are significant surface species results in the following rate expression:

$$r = \frac{kK_1K_{H_2}K_{BNZALD}P_{H_2}P_{BNZALD}}{\left(1 + K_{BNZALD}P_{BNZALD} + K_{H_2}^{1/2}P_{H_2}^{1/2}\right)^2}. \qquad [2]$$

Using a nonlinear regression optimization package (8), this rate expression was applied to the partial pressure data to obtain the fits shown in Fig. 4 and the parameters listed in Table 7. Several other models gave comparable fits to the data, which exhibited some scatter (8), but the parameter values were less consistent. The values of K_{BNZALD} and K_{H_2} in Table 7 represent adsorption equilibrium constants. The former are all larger than the K_{H_2} values; they agree within a factor of 3, and they imply much higher BNZALD coverages, compared to hydrogen, while the latter values show a 50-fold variation. The adsorption constants for Pt powder are noticeably dissimilar to those for supported Pt. The K_{H_2} values are smallest, implying the lowest coverages of hydrogen for the two catalysts with the highest TOFs–Pt powder and Pt/TiO_2 (HTR). The reaction sequence given by [1a]–[1e] is the same as that proposed for acetone hydrogenation on Pt (4), whereas the assumption of noncompetitive hydrogen adsorption along with a more complicated sequence of steps was required to accurately describe benzene and toluene hydrogenation on Pt (37). This is consistent with the hypothesis that BNZALD adsorption occurs primarily via the carbonyl group and the aromatic ring is oriented away from the metal surface, as proposed for cinnamaldehyde (38, 39). This steric consideration would be most prevalent at high surface coverages.

TABLE 7

Regressed Values for the Parameters in Rate Equation [2]

Catalyst	kK_1 (s^{-1})	K_{BNZALD} (atm^{-1})	K_{H_2} (atm^{-1})
Pt/SiO_2	0.08	330	2
Pt/η-Al_2O_3	0.01	400	10
Pt/TiO_2 (LTR)	0.04	580	7
Pt/TiO_2 (HTR)	4.4	310	0.7
Pt powder	1.1	180	0.2

SUMMARY

The specific activity for BNZALD hydrogenation can be significantly increased and the product distribution during this reaction can be markedly altered at high conversions to favor BNZALC by the appropriate choice of the support. Pt/TiO_2 (HTR) was the most active of all the Pt catalysts examined for BNZALD hydrogenation; i.e., activities and TOFs were at least 4–10 times higher than those for Pt/SiO_2 and Pt/η-Al_2O_3, and Pt/TiO_2 (HTR) retained 100% selectivity to BNZALC at conversions up to at least 80%. This behavior of TiO_2-supported Pt can again be explained by invoking special sites created at the metal–support interface which activate the carbonyl bond and enhance its reactivity with hydrogen; however, inhibition of the adsorption of reactive intermediates is also involved. At low conversions (below 20%), BNZALC was the only product formed over any of these Pt catalysts; however, toluene was obtained at higher conversions and benzene was found in small amounts at temperatures greater than 373 K. Hydrogenation of BNZALC showed that benzene is produced only by the hydrogenolysis of BNZALD and only toluene is formed from BNZALC and hydrogen. Pt/TiO_2 (LTR) showed a high selectivity to toluene of over 40% at high conversions. The hydrogenation rates of pure BNZALD and pure BNZALC were similar over Pt/η-Al_2O_3 and Pt/TiO_2 (LTR), but the rate of the latter reaction was suppressed over Pt/TiO_2 (HTR). This is the first time such a reduction in specific activity has been observed in a hydrogenation reaction over Pt/TiO_2. Thus particularly high selectivity to BNZALC over Pt/TiO_2 (HTR) appears to be a result not only of very low surface coverage of BNZALC, but also of a lower specific activity for BNZALC hydrogenation. A simple Langmuir-Hinshelwood model, with the addition of the second hydrogen atom as the rds, fits the data satisfactorily and has the most consistency regarding adsorption parameters.

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