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RESEARCH NOTE

Benzaldehyde Hydrogenation over Titania-Covered Pt Powder

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Titania when used as a support has been found to have a significant effect on the activity and selectivity of Pt during the hydrogenation of aldehydes and ketones (1–7). Turnover frequencies based on hydrogen adsorption sites are markedly enhanced, and rates per gram Pt (at similar dispersions) are also often increased. Perhaps more importantly, with more complex molecules containing both a carbonyl group and unsaturated $C{=}C$ bonds, not only is the rate of hydrogenation of the carbonyl bond enhanced, but the selectivity to unsaturated alcohols is also greatly increased and maintained, even at high conversions. Such products have value as fine chemicals and chemical intermediates. This same behavior has again been demonstrated recently for benzaldehyde hydrogenation over Pt dispersed on SiO_2, Al_2O_3, and TiO_2 (6), and the model favored to explain this kinetic behavior—the creation of special active sites at the titania–metal interface which can polarize and activate the carbonyl bond (8)—was again found to be applicable.

Although we, as well as others, favor this model, there are other possible explanations to account for this performance, at least partially. The most prominent of these are (1) a change in the electronic properties of the Pt caused by electron transfer from (to) the support, (2) a change in the morphology of the Pt crystallites after a high-temperature reduction, and (3) hydrogen spillover onto the support. In an effort to determine the validity of these other explanations, and hopefully to eliminate them as possibilities, a UHP Pt powder was studied before and after the addition of varying amounts of TiO_2 on its surface, and a physical mixture of this powder plus TiO_2 was also examined and compared both to these catalysts and to Pt dispersed on TiO_2. The results are as follows.

The reactor and chemisorption systems have been described in detail previously (3–6). The UHP Pt powder (Puratronic grade, 99.999%, Aesar) had impurity levels of 3 ppm Pd and 7 ppm Rh. The titanium (IV) *n*-nonylate, Ti $(C_9H_{19}O)_4$, was obtained from Alfa, whereas the benzaldehyde (99.98%) and benzyl alcohol (99.98%) were obtained from Aldrich and stored under nitrogen. The H_2 and He (MG Ind., 99.999%) were each passed through a molecular sieve trap (Supelco) and an Oxytrap (Alltech Assoc.). Two TiO_2-promoted Pt catalysts were prepared by dissolving either 0.009 g or 0.08 g Ti nonylate in 6 cm^3 of *n*-pentane and then adding 3 g Pt powder and evaporating the solvent to deposit either 1 or 10 theoretical monolayers of TiO_2 on the surface; these catalysts are respectively designated TiO_x/Pt ($\theta = 1$) and TiO_x/Pt ($\theta = 10$). Both samples were calcined in flowing air (1 SCFH) at 673 K for 2 h to convert the Ti nonylate to Ti oxide and then stored in a desiccator. The $Pt + TiO_2$ (phys. mix) sample was prepared by mixing together 0.13 g Pt powder and 0.094 g TiO_2 to give a composition of 59 wt% Pt.

The pure Pt powder was calcined in a 20% O_2, 80% He mixture at 673 K for 1 h and then reduced in flowing H_2 at 723 K for 1 h prior to either reaction or chemisorption measurements, whereas the two TiO_x/Pt catalysts and the physical mixture of Pt powder plus TiO_2 were given the previously used high temperature reduction (HTR) pretreatment, which included heating under flowing H_2 at 773 K for 1 h (5, 6). As before, H_2 and CO isotherms were extrapolated to zero pressure to correct for adsorption on the titania (1–6). Significant initial deactivation of the pure Pt powder often occurred, but diluting the Pt powder with pure SiO_2 helped to ameliorate this problem. Arrhenius runs were conducted between 353 and 393 K at atmospheric pressure with a benzaldehyde (BNZALD) or a benzylalcohol (BNZALC) partial pressure of 3 Torr, keeping conversions below 20%. The data for the selectivity vs. conversion plots required the use of temperatures from 353 to 503 K to obtain the wide range of conversion desired (up to 80%). One run was conducted at 9 Torr BNZALD.

The surface areas calculated for the clean Pt powder from N_2 BET and H_2 chemisorption measurements were in good agreement, as shown in Table 1, and the average particle size based on the BET area is 670 nm. The addition of TiO_2 to the Pt powder did not change the total surface area, within

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TABLE 1

Adsorption on Pt Catalysts

Catalyst	BET surface area (m^2/g)	H_2 chemisorption (μmole/g)		Irreversible CO chemisorption (μmole/g)
		Irrev	Total	
Pt powder	0.42 (0.38)[a]	2.2	3.8	3.7
TiO_x/Pt ($\theta = 1$) (monolayer)	0.40	1.4	2.6	2.6
TiO_x/Pt ($\theta = 10$) (multilayer)	0.43	0.9	1.9	2.4

[a] Based on total H_2 uptake assuming 1.2×10^{19} Pt_{surf}/m^2.

experimental uncertainty, but it did decrease irreversible chemisorption, especially for hydrogen.

Arrhenius plots for four Pt powder-based catalysts are provided in Fig. 1, while rates, turnover frequencies based on total H_2 adsorption, and activation energies for both BNZALD disappearance and BNZALC formation are given in Table 2. Two supported Pt catalysts studied earlier (6) are also included for comparison. Under differential reaction conditions, BNZALC and toluene (TOL) were the only products detected. The addition of TiO_x to the Pt powder clearly enhanced the rate, increasing it over threefold in the TiO_x/Pt ($\theta = 10$) catalyst, whereas the TOF was enhanced more than sixfold and approached the value for the highly dispersed Pt/TiO_2 catalyst when normalized to Pt_{surf} atoms. At 3 Torr BNZALD, activation energies for BNZALD consumption were near 7 kcal/mole for Pt in the absence of TiO_2, and they were higher in the Pt/TiO_2 and TiO_x/Pt catalysts, increasing to a value near 11 kcal/mole for the TiO_x/Pt ($\theta = 10$) sample.

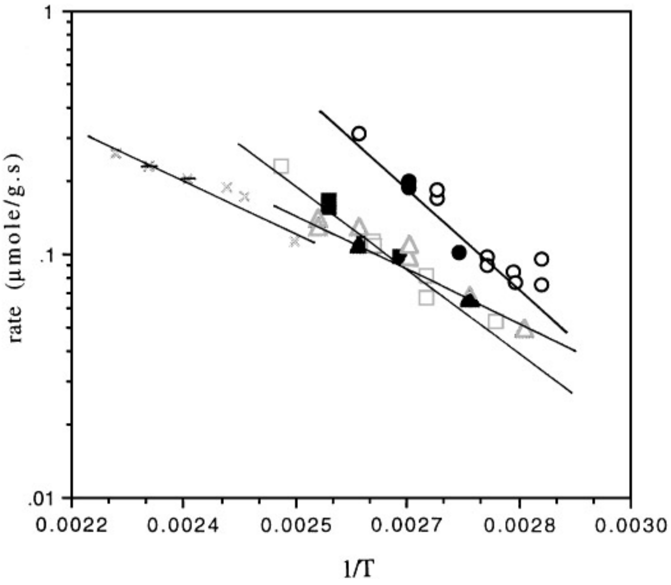

FIG. 1. Arrhenius plots for benzaldehyde hydrogenation over Pt catalysts. $P_{H_2} = 750$ Torr, $P_{BNZALD} = 3$ Torr: (○) Titania/Pt ($\theta = 10$, multilayer), (□) Titania/Pt ($\theta = 1$, monolayer), (△) Pt powder, and (x) Pt powder + TiO_2 (physical mixture, rate per gram Pt); open symbols—ascending T, filled symbols—descending T.

Figure 2a–d shows how selectivity varied with conversion, with the latter variable governed by reaction temperature in this case; consequently, effects caused by either

TABLE 2

Steady-State Benzaldehyde Hydrogenation over Pt Catalysts at 393 K: $P_{BNZALD} = 3$ Torr, $P_{H_2} = 750$ Torr

Catalyst	Activation energy (kcal/mole)[a] BNZALD reacted	Activation energy (kcal/mole)[a] BNZALC formed	Rate $\left(\frac{\mu\text{mole BNZALD}}{\text{s}\cdot\text{gcat}}\right)$	TOF (s^{-1})	Conv. (%)
Pt powder	6.7 ± 0.5	6.6 ± 1.0	0.13	0.017	5–20
TiO_x/Pt ($\theta = 1$) (monolayer)	9.9 ± 0.7	8.2 ± 1.0	0.20	0.039	5–20
TiO_x/Pt ($\theta = 10$) (multilayer)	9.4 ± 2.3	10.8 ± 2.4	0.42	0.110	7–20
TiO_x/Pt ($\theta = 10$) (multilayer)[b]	11.2 ± 1.7	11.8 ± 1.3	0.63	0.165	7–25
Pt + TiO_2 (phys. mix)	6.0 ± 0.9	7.6 ± 1.1	0.08[c]	0.011	8–25
0.96% Pt/SiO_2[d]	7.2 ± 0.8	7.2 ± 0.8	1.41	0.028	11–20
0.65% Pt/TiO_2 (HTR)[d]	8.2 ± 0.7	8.2 ± 0.7	4.50	1.07 (0.135)[e]	12–24

[a] With 95% confidence interval.
[b] $P_{BNZALD} = 9$ Torr.
[c] Per gram Pt powder.
[d] From Ref. 6.
[e] Value in parentheses based on Pt dispersion of unity.

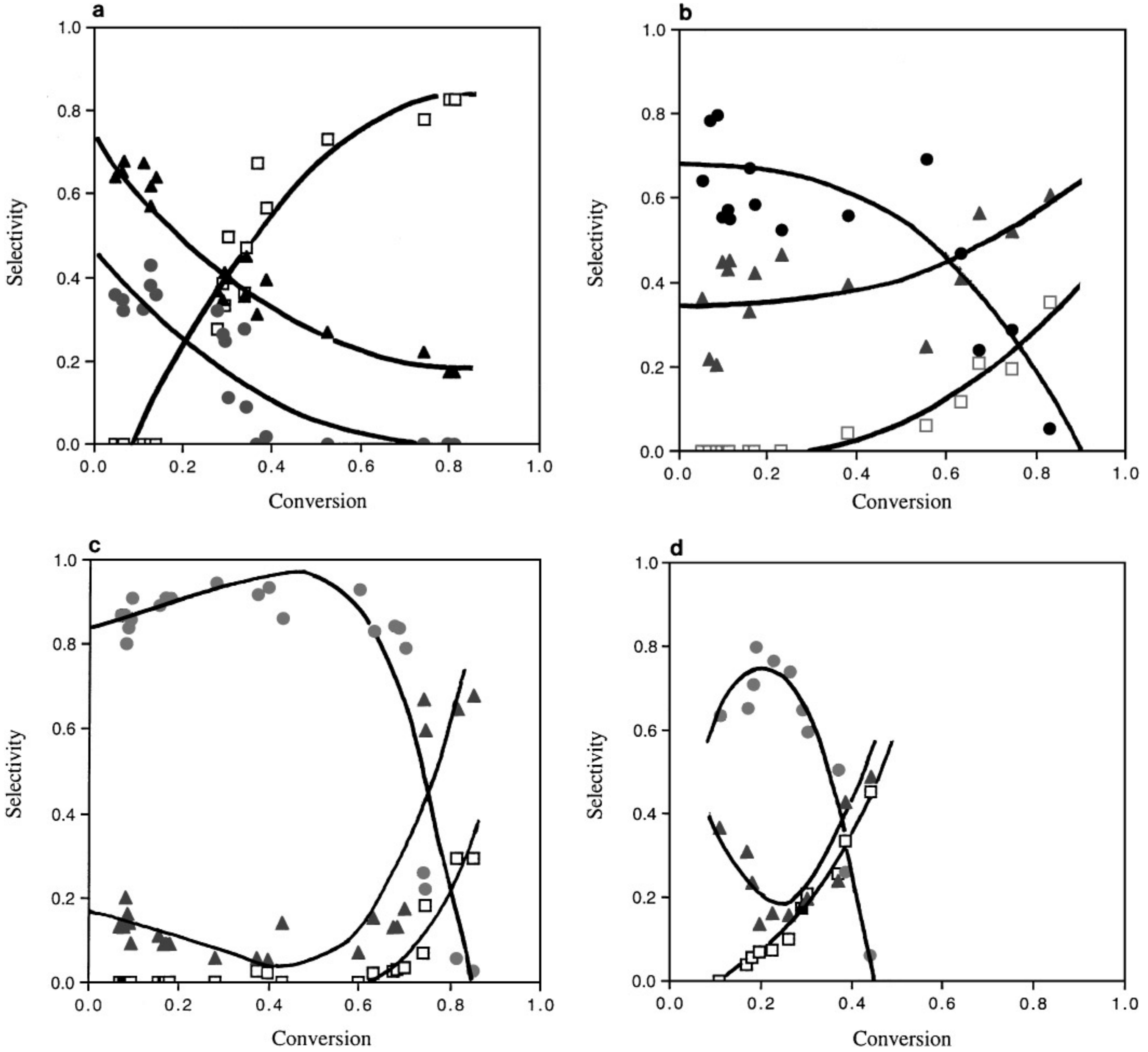

FIG. 2. Selectivity vs. conversion for benzaldehyde hydrogenation; $P_{\mathrm{H_2}} = 750$ Torr, $P_{\mathrm{BNZALD}} = 3$ Torr, $T = 353$–523 K: (●) benzyl alcohol, (▲) toluene, (□) benzene. (a) Pt powder, (b) $\mathrm{TiO_x/Pt}$ ($\theta = 1$), (c) $\mathrm{TiO_x/Pt}$ ($\theta = 10$), (d) Pt powder + $\mathrm{TiO_2}$ (physical mixture).

conversion or temperature cannot be separated under clearly nondifferential conditions. Regardless, relative comparisons among these four catalysts are valid and informative because experimental conditions were similar. As with the dispersed Pt catalysts (6), BNZALC selectivity was highest with the $\mathrm{TiO_x/Pt}$ catalysts, and it was maintained at high conversions; for example, the ($\theta = 10$) sample gave a product containing 80 mole% BNZALC up to conversions approaching 70%. Compared to the pure Pt powder, the $\mathrm{TiO_x/Pt}$ ($\theta = 10$) sample also demonstrated a marked enhancement in BNZALC formation, although the selectivity began dropping at much lower conversions. There was absolutely no enhancement in either rate or TOF for the Pt powder in the physical mixture with $\mathrm{TiO_2}$, but an increase in BNZALC selectivity at low conversions was observed. Hydrogenolysis activity was clearly greatest with the Pt powder and Pt powder/$\mathrm{TiO_2}$ mixture and became noticeably significant at conversions above 30%, whereas for the $\mathrm{TiO_x/Pt}$ ($\theta = 10$) sample, it was completely suppressed until conversions rose above 60%.

With Pt particles this large (0.67 μm), no significant changes in surface morphology should occur, and Pt(111) planes should dominate. This was verified by DRIFTS studies of CO adsorbed on these samples, which gave a peak near 2087 cm^{-1} indicative of CO on a Pt(111) surface, which is expected to denominate on large crystallites (9). Furthermore, no change in the Fermi level of these large Pt crystallites will occur when in contact with a semiconductor oxide. Previous studies of Pt dispersed on TiO_2 have repeatedly shown that the decrease in chemisorption capacity after an HTR step is a result of physical blockage caused by migrating TiO_x species (10, 11). Blockage of the Pt surface by TiO_x is the obvious explanation for the decreased adsorption shown in Table 1. The greater effect on H_2 adsorption is most likely the result of a requirement of site pairs for dissociative adsorption compared to the single-site, atop CO adsorption mode.

The rate enhancement upon addition of TiO_x to the Pt surface cannot be attributed to an increase in surface area, as shown in Table 1, or to a change in bulk electronic properties or to a change in surface morphology. These results provide overwhelming evidence against the first two possible explanations mentioned earlier. The role of hydrogen spillover cannot be unequivocally discounted, but the absence of a rate enhancement or a change in the activation energy when Pt powder was physically mixed with TiO_2 powder argues strongly against any significant effect. Again, the most consistent model is that proposing the formation of new active sites at the Pt–titania interface at which Ti^{3+} cations and/or oxygen vacancies can polarize and active the carbonyl bond (8). Evidence for this has been provided by Bonneviot and Haller (12) and by Munuera and co-workers (13, 14). At the higher temperatures used in HTR, H_2 spillover can facilitate this process of oxygen removal (15). As before, one of the strongest arguments favoring this explanation is the increase in activation energy as the rate increases, thus forcing the pre-exponential factor, which contains the active site density, to be completely responsible for the activity enhancements.

Perhaps more compelling than the enhancements in rate and TOF is the replication of high BNZALC selectivity that was observed previously with dispersed Pt/TiO_2 (HTR) catalysts, particularly at high conversion (6). The data in Fig. 2 show clearly that the addition of titania enhances selectivity to BNZALC, and this increase is maintained to conversions above 70%. This marked improvement is most evident with the TiO_x/Pt ($\theta = 10$) catalyst, and similar behavior occurred at a BNZALD pressure of 9 Torr (16). Another important feature to point out is the inhibition in benzene (BZ) formation upon addition of titania, again in agreement with results for dispersed Pt/TiO_2 catalysts (6). The hydrogenation of BNZALD to form BNZALC and TOL are reactions that occur in series, whereas BZ formation is a parallel reaction resulting from BNZALD hydrogenolysis (6), and it occurs readily on Pt powder (see Fig. 2a). Because hydrogenolysis reactions are typically structure-sensitive, requiring ensembles of many atoms (17, 18), the presence of TiO_x species on the Pt surface breaks up these ensembles and markedly decreases the rates of hydrogenolysis reactions (11). Consequently, the inhibited formation of BZ can be readily explained by this ensemble effect.

As discussed elsewhere in detail (6), the selectivity to BNZALC is not only high, but it is retained at high conversions with the TiO_x/Pt catlysts; consequently, the adsorption properties as well as the kinetic behavior must have been altered because toluene cannot form unless BNZALC readsorbs on the catalyst. The results indicate that the presence of TiO_x on the Pt surface inhibits BNZALC adsorption relative to BNZALD, thus maintaining a surface covered almost completely with the latter, even at high concentrations of BNZALC (i.e., at high conversions). However, hydrogenation of a pure BNZALC feed has produced TOFs that are lower than those for BNZALD on a well-dispersed Pt/TiO_2 (HTR) catalyst, whereas similar values were obtained with Pt/TiO_2 (LTR) and Pt/Al_2O_3 (6). Thus in this reaction a lower specific rate constant also favors selectivity to BNZALC.

The question as to whether crystallite size effects exist in this type of hydrogenation reaction has not yet been resolved. Lercher and co-workers recently reported that crotyl alcohol selectivity during crotonaldehyde hydrogenation was higher over large Pt crystallites (7); however, studies with other metal catalysts have produced conflicting results related to the hydrogenation of other aldehydes and ketones which also contain unsaturated C=C bonds (5). The similarity in the selectivity vs. conversion plots after HTR for the TiO_x/Pt ($\theta = 10$) sample with 670-nm particles and the 0.65% Pt/TiO_2 catalyst with 1-nm particles (see Ref. 6) strongly implies that no significant crystallite size effect exists in this hydrogenation reaction. The near agreement in TOF values from these two samples when based on the actual dispersion of the 0.65% Pt/TiO_2 catalyst (i.e., the Pt_{surf}/Pt_{total} ratio) is another indication of the absence of a crystallite size effect; consequently, we do not believe that crystallite size effects play a significant role in the BNZALD hydrogenation reaction over Pt.

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