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The influence of MSI (metal–support interactions) on phenylacetaldehyde hydrogenation over Pt catalysts

D. Poondi, M.A. Vannice *

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

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Abstract

TiO₂-supported Pt, after a high-temperature reduction (HTR) at 773 K to induce the SMSI state, had a turnover frequency (TOF) for phenylacetaldehyde hydrogenation that was 15–20 times higher than TOF values for Pt dispersed on either SiO₂ or η -Al₂O₃ and, since all supported catalysts had Pt dispersions of unity (1 nm crystallites), the TOF for Pt/TiO₂ (HTR) based on complete dispersion was still 2–5 times greater than the other supported catalysts. More importantly, selectivity to 2-phenylethanol was markedly enhanced over Pt/TiO₂ (HTR), comprising 70% of the product at conversions as high as 60%. Pt/TiO₂ after a low temperature reduction (LTR) at 473 K gave neither the high TOFs nor the enhanced selectivity. Among these catalysts the highest activation energy of 12.4 kcal/mol was attained with Pt/TiO₂ (HTR) and the reaction order on phenylacetaldehyde was between 0 and 1/2 while that on H₂ was around 1/2 or higher. At higher conversions (over 50%) significant hydrogenolysis activity to form benzene and toluene occurred on all Pt catalysts except Pt/TiO₂ (HTR). The higher hydrogenation activity and suppressed hydrogenolysis capability with the Pt/TiO₂ (HTR) catalyst is attributed to TiO_x species migrating onto the Pt surface to create active sites at the Pt–titania interface while simultaneously destroying large ensembles of Pt atoms required for hydrogenolysis reactions; however, competitive desorption/readsorption processes must also play a significant role in enhancing selectivity to the intermediate phenylethanol product.

Keywords: Metal–support interactions; Platinum/titania; Phenylacetaldehyde hydrogenation; Phenylethanol

1. Introduction

Two challenges in the manufacture of fine chemicals are to reduce energy and raw materials consumption and to produce minimal unwanted environmental waste [1]. The hydrogenation of ketones or aldehydes containing unsaturated C=C bonds to an alcohol is a class of reactions important to specialty chemicals

and enhancing activity, and controlling selectivity to favor the desired product impacts directly on the above latter goal.

Hydrogenation of aromatic aldehydes and ketones has been studied over supported Pt catalysts in both the vapor and liquid phases [2–12]. Dispersing Pt on titania has been found to enhance activity for hydrogenating molecules containing a C=O bond [2,3,13] and furthermore, the use of Pt/TiO₂ increased the selectivity to benzyl alcohol and 1-phenylethanol during the respective hydrogenation of benzaldehyde and acetophenone while it also suppressed hy-

* Corresponding author. Tel.: +1-814-8634803; fax: +1-814-8657846; e-mail: mavche@enr.psu.edu.

drogenolysis reactions [2,3]. The deposition of titania on large (760 nm) Pt crystallites resulted in similar improved performance [14]. The enhanced activity for hydrogenation of the carbonyl bond over these Pt/titania systems has been attributed to the activation of this bond by defect sites on the oxide created at the Pt–titania interface [13], while the reduced hydrogenolysis activity has been explained by the destruction of large ensembles of metal atoms by migrating TiO_x species [3,14].

Vapor-phase hydrogenation of ketones such as acetophenone, methyl benzyl ketone and ethyl phenyl ketone over Pd/SiO₂ at 298 K showed that total conversion was not significantly affected by the location of the C=O bond relative to the aromatic ring in these molecules; however, selectivity to the aromatic alcohol was higher during hydrogenation of ethyl benzyl ketone and methyl phenyl ketone compared to the hydrogenation of acetophenone [15]. A similar study of aromatic aldehydes could determine the influence of the location of the aromatic ring, relative to that of the aldehyde group, on activity and selectivity. A study of benzaldehyde hydrogenation has recently been completed [3] and a similar investigation of phenylacetaldehyde hydrogenation over the same family of Pt catalysts is described here. Consequently, when combined with our earlier studies [2,3], the hydrogenation behavior of benzaldehyde, acetophenone, and phenylacetaldehyde over Pt can now be compared.

2. Experimental

The Pt powder was Puratronic grade (Johnson Matthey, 99.999%) which was heated in O₂ at 673 K prior to pretreatment in H₂. The dispersed Pt catalysts were prepared by an incipient wetness technique using H₂PtCl₆ (Aldrich, 99.995%) dissolved in distilled, deionized water along with either $\eta\text{-Al}_2\text{O}_3$ (from alumina β -trihydrate calcined at 873 K, 150 m²/g) or TiO₂ (Degussa P25, 40 m²/g). Pt/SiO₂ had

been prepared by an ion-exchange method using SiO₂ (Davison grade 57, 220 m²/g) and Pt(NH₃)₄Cl₂ (Strem, 55.3% Pt) as a precursor [2]. All support materials were calcined at 773 K in air for 2 h before impregnation. The impregnated catalysts were dried at 393 K overnight and stored in a desiccator for later use. One of three pretreatment procedures described previously [3] was followed prior to either chemisorption measurements or the kinetic studies; in brief, the Pt/SiO₂ and Pt/ $\eta\text{-Al}_2\text{O}_3$ samples were reduced at 723 K, the LTR (low temperature reduced) Pt/TiO₂ sample was reduced at 473 K and the HTR (high temperature reduced) Pt/TiO₂ sample was reduced at 773 K [3]. The chemisorption system produced a vacuum below 10⁻⁶ Torr at the sample and has been described previously [16].

Phenylacetaldehyde (Sigma, 97%) was stored under nitrogen below 270 K in a freezer. The 2-phenylethanol (Aldrich, 99 + %) was stored in a glove bag purged with nitrogen. Hydrogen and helium (MG Ind., UHP grade, 99.999%) were passed through both molecular sieve traps (Supelco) and Oxytraps (Alltech Asso.). A mixture of phenylacetaldehyde (PhAc) and H₂ at atmospheric pressure and a total flow rate of 50 sccm was passed through a Pyrex reactor containing 20–40 mg of catalyst which was heated in a fluidized sand bath. PhAc partial pressures and reactor line temperatures were chosen to eliminate condensation, thus the PhAc partial pressure was typically maintained at 3 Torr, but reaction at 4.5 and 6 Torr was also studied. The preheater line, the gas sampling valve and all the lines downstream from the reactor were kept at 473 K. Some 2-phenylethanol (PhEt) decomposed to styrene during passage through the lines to the gas chromatograph and reducing the line temperature decreased this decomposition, but did not completely eliminate it. The effluent gas was analyzed by a gas chromatograph (H-P 5890 Series II) with a single TC detector and a 10 ft Carbowax 20M column. The oven temperature program was typically initiated at 358 K, ramped at 35 K/min to 473 K, then held at that

temperature for 20 min. A 3 ft Chromosorb 102 column was later used to separate hydrogenolysis products such as CO and formaldehyde because these products were not separated by the Carbowax 20M column. With the Chromosorb 102 column the oven temperature was held initially at 228 K for 6 min, ramped at 50 K/min to 493 K and held at that temperature for 7 min.

3. Results

Hydrogen chemisorption was used to characterize both supported and unsupported Pt catalysts, and the uptake, Pt dispersion and Pt crystallite sizes were reported earlier [3]; however, the pertinent results are summarized in Table 1.

A simplified reaction network scheme for phenylacetaldehyde (PhAc) hydrogenation is shown in Fig. 1. 2-Phenylethanol (PhEt), styrene (Sty), ethylbenzene (EtBz), cyclohexylethanal (CyHxal) and cyclohexylethanol (CyHxol) were the products observed during PhAc hydrogenation over these Pt catalysts; however, benzene, toluene, CO and formaldehyde were also produced via hydrogenolysis reactions when Pt powder or Pt/SiO₂ was used. Quantitative analysis of the product stream was complicated by the absence of certain thermal response factors in the literature and these had to be experimentally determined for the TC detector used here.

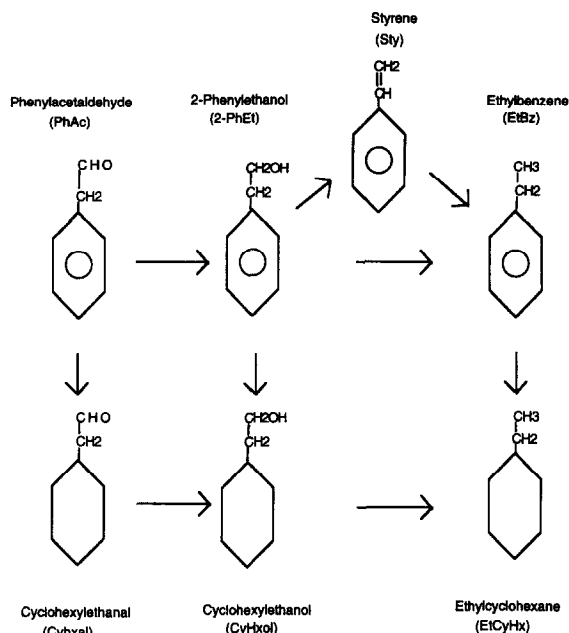


Fig. 1. Reaction pathways during phenylacetaldehyde hydrogenation.

The pure compounds were vaporized in an empty reactor using a given flow of He and nitrogen to establish a known partial pressure for each component, and the response factor for the desired compound was then calculated using nitrogen as a reference peak [14]a. The elution times and response factors for PhAc and other products are listed in Table 2.

The first measurement of PhAc hydrogenation activity could not be made until 90 min

Table 1
Characterization of Pt catalysts by chemisorption at 300 K

Catalyst	T_{red} (K)	H_2 chemisorption ($\mu\text{mol } H_2/\text{g cat}$) (H_{Tot}/Pt_{Tot})		d^a (nm)
		irrev	total	
0.96% Pt/SiO ₂	723	19.0	28.0	1.14
0.78% Pt/ η -Al ₂ O ₃	723	13.0	22.0	1.09
0.65% Pt/TiO ₂ (LTR)	473	12.0	22.0	1.37
0.65% Pt/TiO ₂ (HTR)	773	1.1	2.1	0.12
		5.0 ^b	40.0 ^b	0.15 (CO/Pt)
0.24% Pt/SiO ₂ -Al ₂ O ₃	448	3.0	7.0	1.15
Pt powder	723	1.7	3.1	0.0012

^a Average Pt crystallite size.

^b CO chemisorption.

Table 2
Elution time and response factor for products from phenylacetaldehyde hydrogenation (with a Carbowax 20M column)

Compound	Residence time (min)	Response factor	Ref.
CO	0.71 ^a	42	[35]
Benzene	1.85	100	[35]
Toluene	2.25	116	[35]
Ethylbenzene	2.60	129	[35]
Styrene	3.20	113 ± 12	this study
Cyclohexylethanal	4.03	130 ± 12	this study
Cyclohexylethanol	4.52	116 ± 12	this study
Phenylacetaldehyde	5.30	122 ± 6	this study
2-Phenylethanol	7.58	140 ± 11	this study
Formaldehyde	7.70 ^a	65	[36]

^a Residence time in 3 ft Chromosorb 102 column (see Section 2).

after the introduction of the reactant because of the long time necessary for stabilization of the PhAc pressure due to the very low flow rates. After these early activity measurements, Arrhenius runs were conducted with an effort to keep conversions below 20%; however, when higher conversions were attained with Pt powder and Pt/TiO₂ (LTR), the mass balance equation for an integral reactor was used to evaluate rate constants and apparent activation energies assuming a half-order dependence on H₂ and a zero-order dependence on PhAc. Representative Arrhenius plots are shown in Fig. 2. Calculations using the Weisz criterion [17] showed that no mass transfer limitations should exist [14]. The rates, activation energies and TOFs for PhAc consumption at 3 Torr and 423 K are listed in Table 3. The apparent activation energies varied from 2.4 to 12.4 kcal/mol and TOFs based on hydrogen chemisorption ranged from 0.020 to 0.833 s⁻¹. The TOF value for

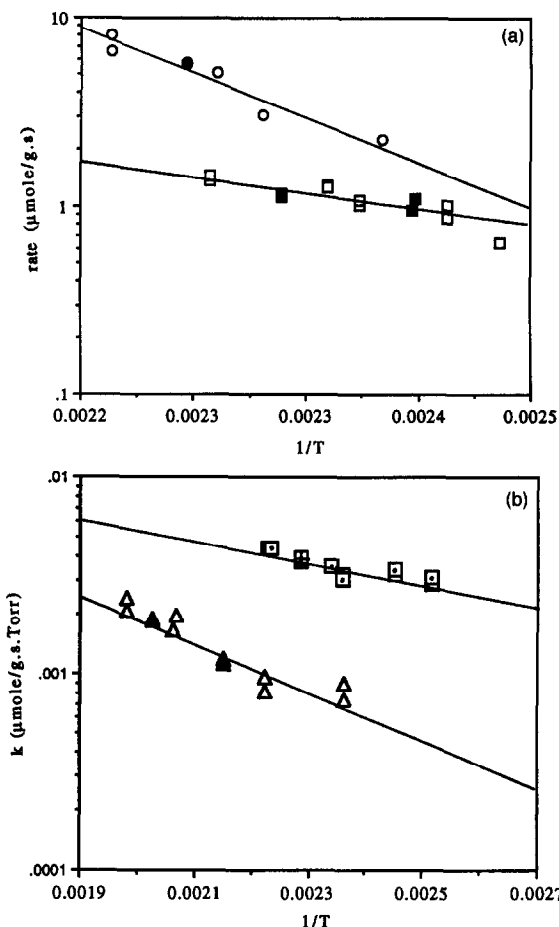


Fig. 2. Arrhenius plots for phenylacetaldehyde hydrogenation over Pt Catalysts; $P_{\text{PhAc}} = 3$ Torr, $P_{\text{H}_2} = 750$ Torr, open symbols, ascending T; closed symbols, descending T: (a) 0.78% Pt/ η -Al₂O₃ (□), 0.65% Pt/TiO₂ (HTR) (○); (b) 0.65% Pt/TiO₂ (LTR) (Δ), Pt powder (□).

Pt/TiO₂ (HTR) listed in parentheses was obtained by normalizing the rate to the dispersion of the LTR catalyst (i.e., 100%), thus it represents a minimum TOF value. The TOF for Pt

Table 3

Kinetic parameters for phenylacetaldehyde hydrogenation on Pt catalysts: $T = 423$ K, $P_{\text{PhAc}} = 3$ Torr, $P_{\text{H}_2} = 750$ Torr

Catalyst	T_{red} (K)	Rate _{PhAc} (μmol/s · g cat)	E^a (kcal/mol)	TOF (s ⁻¹)	Conv. (%)
0.78% Pt/Al ₂ O ₃	723	1.69	6.0 ± 1.1	0.042	11–22
0.96% Pt/SiO ₂	723	2.57	—	0.052	—
0.65% Pt/TiO ₂ (LTR)	473	0.67	5.8 ± 0.7	0.020	19–60
0.65% Pt/TiO ₂ (HTR)	773	3.50	12.4 ± 1.0	0.833 (0.105) ^b	9–25
Pt powder	723	1.82	2.4 ± 0.4	0.294	28–40

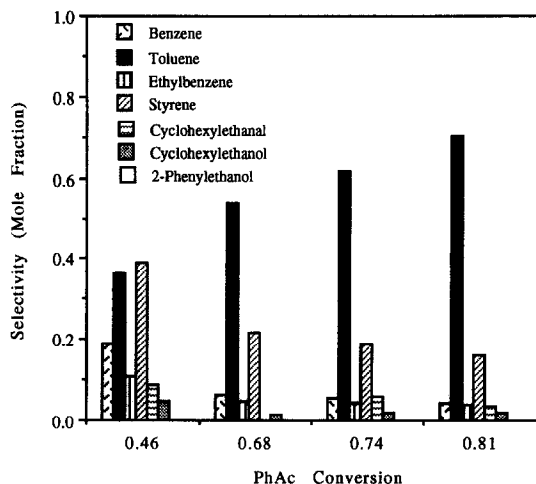
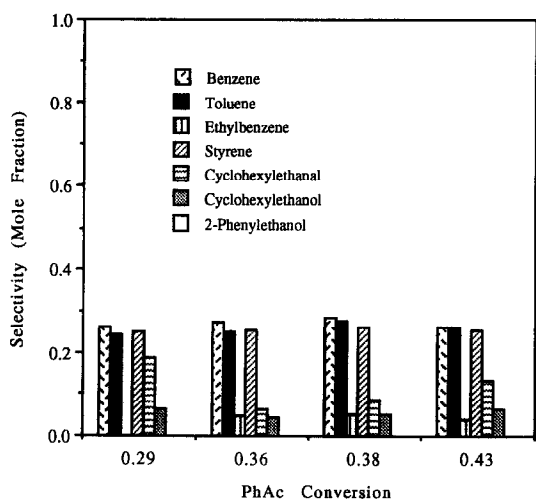
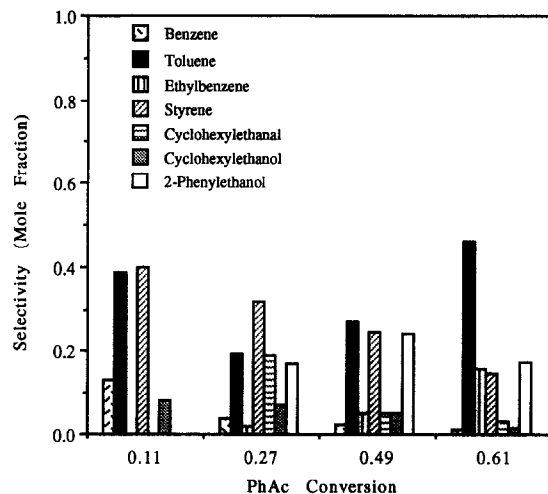
^a With 95% confidence interval.

^b Assuming Pt dispersion of unity.

Table 4

Partial pressure dependencies^a: rate = $kP_{\text{PhAc}}^a P_{\text{H}_2}^b$, $T = 423 \text{ K}$

Catalyst	<i>a</i>	<i>b</i>
Pt powder	0.0 ± 0.04	0.70 ± 0.08
0.78% Pt/ $\eta\text{-Al}_2\text{O}_3$	0.43 ± 0.05	0.42 ± 0.11
0.65% Pt/TiO ₂ (HTR)	0.53 ± 0.16	not determined

^a With 95% confidence interval.Fig. 3. Selectivity at different conversions for phenylacetaldehyde hydrogenation over Pt/SiO₂: $P_{\text{H}_2} = 750 \text{ Torr}$, $P_{\text{PhAc}} = 3 \text{ Torr}$, $T = 423\text{--}513 \text{ K}$.Fig. 4. Selectivity at different conversions for phenylacetaldehyde hydrogenation over Pt powder: $P_{\text{H}_2} = 750 \text{ Torr}$, $P_{\text{PhAc}} = 3 \text{ Torr}$, $T = 403\text{--}523 \text{ K}$.Fig. 5. Selectivity at different conversions for phenylacetaldehyde hydrogenation over Pt/ $\eta\text{-Al}_2\text{O}_3$: $P_{\text{H}_2} = 750 \text{ Torr}$, $P_{\text{PhAc}} = 3 \text{ Torr}$, $T = 423\text{--}513 \text{ K}$.

powder was higher than those for Pt/SiO₂ and Pt/ $\eta\text{-Al}_2\text{O}_3$ indicating a possible crystallite size effect. Partial pressure dependencies were determined at 423 K and are listed in Table 4. A zero-order dependency on PhAc was obtained for Pt powder compared to respective values of 0.43 and 0.53 for Pt/ $\eta\text{-Al}_2\text{O}_3$ and Pt/TiO₂ (HTR), while dependencies on H₂ pressure were near half-order.

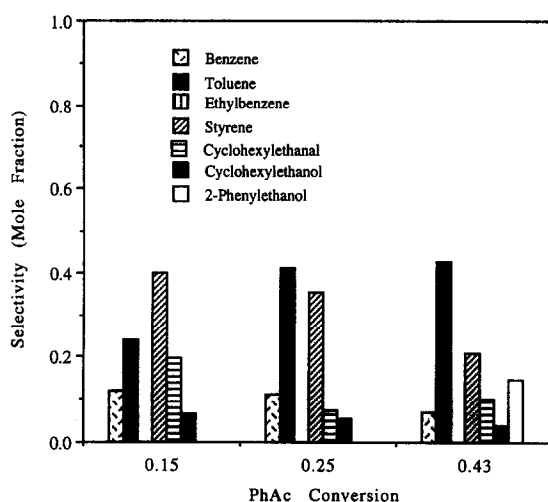
Fig. 6. Selectivity at different conversions for phenylacetaldehyde hydrogenation over Pt/TiO₂ (LTR): $P_{\text{H}_2} = 750 \text{ Torr}$, $P_{\text{PhAc}} = 3 \text{ Torr}$, $T = 423\text{--}503 \text{ K}$.

Table 5

Phenylacetaldehyde hydrogenolysis and hydrogenation activities over Pt catalysts: $P_{\text{PhAc}} = 3$ Torr, $P_{\text{H}_2} = 750$ Torr, $T = 423$ K

Catalyst	Product %		TOF $\times 1000$ (s^{-1})	
	hydrogenolysis	hydrogenation	hydrogenolysis	hydrogenation
Pt/SiO ₂	55	45	29	24
Pt/ η -Al ₂ O ₃	27	73	11	31
Pt powder	51	49	150	143
Pt/TiO ₂ (LTR)	31	69	6	14
Pt/TiO ₂ (HTR)	22	78	181 (23) ^a	652 (82) ^a

^a Value in parentheses based on Pt dispersion of unity.

Figs. 3–7 show selectivity-conversion plots for Pt/SiO₂, Pt powder, Pt/ η -Al₂O₃, Pt/TiO₂ (LTR) and Pt/TiO₂ (HTR) at 3 Torr PhAc and reaction temperatures ranging from 400 to 523 K. Conversions were varied by changing both space velocity and temperature. Styrene was presumably formed by dehydration of 2-PhEt on either Pt or the acidic sites on the support, and in some cases no 2-PhEt was detected in the product stream. The concentration of hydrogenolysis products like toluene and benzene typically increased with conversion and temperature. The selectivity to toluene was higher than that to benzene, except for Pt powder, and the formation of these products was clearly inhibited with the Pt/TiO₂ (HTR) sample.

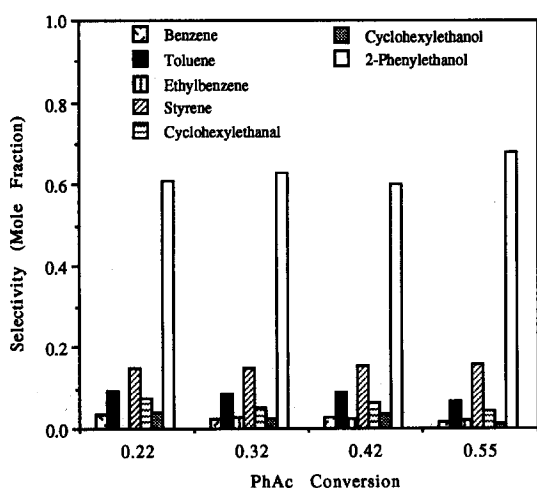


Fig. 7. Selectivity at different conversions for phenylacetaldehyde hydrogenation over Pt/TiO₂ (HTR): $P_{\text{H}_2} = 750$ Torr, $P_{\text{PhAc}} = 3$ Torr, $T = 413$ – 473 K.

Table 5 shows the extent of hydrogenolysis reactions and compares PhAc hydrogenolysis versus hydrogenation over these Pt catalysts, while Table 6 gives the composition of the hydrogenolysis product at three conversions over these Pt catalysts. The reaction temperatures are not too dissimilar, with a maximum temperature difference of 50 K. The hydrogenolysis reactions were clearly suppressed on the Pt/TiO₂ (HTR) sample. The composition of the PhAc hydrogenation products at 3 Torr can be determined from Figs. 3–7. This composition over

Table 6

Hydrogenolysis products at various phenylacetaldehyde conversions (X_{PhAc}): $P_{\text{H}_2} = 750$ Torr, $P_{\text{PhAc}} = 3$ Torr

Catalyst	T_{rxn} (K) ^a	% Hydrogenolysis	% Toluene	% Benzene
$X_{\text{PhAc}} = 0.3$				
Pt powder	423	51	48	52
Pt/ η -Al ₂ O ₃	438	23	83	17
Pt/TiO ₂ (LTR)	465	39	80	20
Pt/TiO ₂ (HTR)	448	11	78	22
$X_{\text{PhAc}} = 0.4$				
Pt/ η -Al ₂ O ₃	453	24	87	13
Pt/TiO ₂ (LTR)	473	50	86	14
Pt powder	448	52	51	49
Pt/TiO ₂ (HTR)	448	12	74	26
Pt/SiO ₂	423	47	66	34
$X_{\text{PhAc}} = 0.6$				
Pt/ η -Al ₂ O ₃	513	47	98	2
Pt/TiO ₂ (LTR)	504	52	92	8
Pt/TiO ₂ (HTR)	468	10	83	17
Pt/SiO ₂	473	52	83	17

^a Reaction temperature.

Pt/ η -Al₂O₃ showed no obvious trends as the PhAc pressure varied from 3 to 6 Torr and the H₂ pressure varied between 500 and 750 Torr [14]a.

4. Discussion

No previous study of PhAc hydrogenation could be found, thus this investigation of vapor-phase PhAc hydrogenation may be the first reported. Studying the vapor-phase reaction of a compound with a relatively low vapor pressure and high reactivity under differential reaction conditions is not a trivial effort; however, this approach does allow determination of catalytic behavior in the absence of any solvent effects. Although low conversions frequently were attained at low temperatures, a wide range of conversion was necessary to compare all catalysts under similar conditions and to evaluate fully the product distributions from these catalysts. Under these reaction conditions one must be aware of not only mass transfer resistances, especially pore diffusion, but also the possibility of capillary condensation of high-boiling compounds. Application of the Weisz criterion routinely gave very low values (ca. 0.02) indicating no significant mass transport limitations [14]a. Since the PhAc vapor pressure temperature dependence could not be found, properties comparable to an isomer, acetophenone, were assumed and the Kelvin equation was applied. The diameter of a pore in which capillary condensation might begin to occur at the lowest temperature used was 2 nm [14]a, which is much smaller than the average pore diameters in these oxide supports, i.e. 6, 14 and 20 nm for η -Al₂O₃, SiO₂ and TiO₂, respectively [14]a.

Catalyst deactivation during the initial 90 min period on stream could not be determined, but Rylander has reported that Pt catalysts deactivate during aliphatic or aromatic aldehyde hydrogenation [18]. The earliest activities for PhAc

hydrogenation were typically determined after 90 min on stream and are listed as steady-state values because little deactivation was observed during the subsequent Arrhenius runs shown in Fig. 2. The apparent activation energies for PhAc conversion at 3 Torr fell between 2 and 12 kcal/mol, a range of values similar to those reported for both acetophenone and benzaldehyde hydrogenation in which cases the respective activation energies varied from 3 to 9 kcal/mol and 5 to 13 kcal/mol under similar reaction conditions [2,3]. These low values are also similar to those obtained for crotonaldehyde, acetone and acetophenone hydrogenation over copper chromite catalysts [19]. All results indicate these represent actual kinetic barriers unaffected by pore diffusion. The product distributions related to benzene, toluene, 2-phenylethanol, cyclohexylethanal, cyclohexylethanol, ethylbenzene and styrene varied significantly for different Pt catalysts and this may help explain the noticeable variations in apparent activation energies.

A comparison of the TOFs given in Table 3, based on the amount of PhAc reacted, clearly shows that Pt/TiO₂ (HTR) is much more active than any other supported Pt catalyst, even if the minimum value is used. The TOF on Pt/TiO₂ (HTR) is higher than that on Pt/TiO₂ (LTR) by a factor varying from a minimum value of 5 to a value of 40 based on hydrogen adsorption sites, and the TOFs among these Pt catalysts varied by over two orders of magnitude, i.e. from 0.020 to 0.833 s⁻¹, when based on sites capable of adsorbing hydrogen at 300 K. Table 5 reports TOFs representing separate hydrogenolysis and hydrogenation reactions of PhAc and the TOF for only hydrogenation reactions on Pt/TiO₂ (HTR) is clearly higher than the TOFs on Pt/SiO₂, Pt/ η -Al₂O₃, and Pt/TiO₂ (LTR), regardless of the basis of calculation. As repeatedly observed in other hydrogenation reactions involving a carbonyl bond [13], this higher activity is not due to a lower activation energy and, in fact, the E_a value for Pt/TiO₂ (HTR) is twice that for the other supported Pt catalysts.

Higher TOFs for benzaldehyde and acetophenone hydrogenation on Pt/TiO₂ (HTR) have also been obtained [2,3] and Coq et al. found that Ru/TiO₂ (HTR) showed higher rates for liquid-phase cinnamaldehyde hydrogenation at 333 K compared to Ru/SiO₂ [11].

Hydrogenation of the aromatic ring in PhAc to CyHxal is more thermodynamically favored than hydrogenation of the carbonyl bond to give 2-PhEt; however, the results obtained here, along with those obtained previously for hydrogenation of benzaldehyde and acetophenone [2,3], show that ring hydrogenation is less likely to occur on Pt and reduction of the carbonyl group is favored in most cases. The reasons why the aromatic ring is far less reactive with hydrogen than the carbonyl bond are not clear, but they may be due to both the orientation of PhAc adsorbed on the surface and an electronic effect on the reactivity of the aromatic ring caused by the C=O bond in the molecule. The structural configuration of adsorbed PhAc has not been investigated; however, Gallezot et al. have proposed an adsorption configuration for cinnamaldehyde with the carbonyl bond attached to the surface and the aromatic ring oriented away from the surface [12]. Delbecq and Sautet have assumed that the aromatic ring is oriented away from the surface whereas the reactive C=C and C=O bonds in cinnamaldehyde are involved in chemisorption, and they used semiempirical calculations to estimate binding energies on Pt and Pd [20]. No hydrogenation of the aromatic ring was detected during benzaldehyde hydrogenation over Pt(3) and limited ring hydrogenation was observed with acetophenone [2,21]. Based on the studies of these French workers, it has been suggested that on a nearly saturated surface benzaldehyde might be forced to adsorb with the carbonyl bond interacting with the surface while the aromatic ring is oriented away because of a crowding effect [3,14] and a similar situation may exist with PhAc. Regardless, because hydrogenation of the C=O bond in PhAc to form 2-PhEt is not the thermodynamically favored route, the selectivity to PhEt must

be kinetically controlled, which would involve both intrinsic rate constants and equilibrium adsorption constants. The alternative initial reaction pathway of ring hydrogenation of PhAc to CyHxal, which is subsequently hydrogenated to CyHxol, is obviously inhibited.

PhEt can be dehydrated to form styrene, a reaction whose free energy change becomes negative near 420 K. The dehydration of 1-PhEt to styrene during acetophenone hydrogenation has already been observed over acid sites on the support surface [2]. In the present study, significant concentrations of styrene were measured in the product stream during PhAc hydrogenation over Pt powder as well as the supported Pt catalysts, thus implying that 2-PhEt dehydration to styrene can occur on Pt as well as the support oxides and the styrene can then be hydrogenated on Pt to yield EtBz. At low conversions, the PhEt produced in the reaction over Pt/SiO₂, Pt/TiO₂ (LTR) and Pt/ η -Al₂O₃ was either desorbed as a product or dehydrated to styrene and no EtBz was detected; however, the selectivity to EtBz increased at higher conversions when the PhEt and styrene concentrations became higher. More importantly, secondary hydrogenation to EtBz was suppressed over Pt/TiO₂ (HTR) for conversions ranging up to 60%. In similar fashion, secondary hydrogenation of benzyl alcohol to toluene was also suppressed over Pt/SiO₂, Pt/TiO₂ (LTR) and Pt/ η -Al₂O₃ at low benzaldehyde conversions (< 20%), whereas no toluene was detected over Pt/TiO₂ (HTR) at conversions up to 80% [3]. The high selectivity to benzyl alcohol at low conversions over Pt/TiO₂ (LTR) and Pt/ η -Al₂O₃ was clearly attributable to low surface coverages of benzyl alcohol because the TOFs for benzaldehyde and benzyl alcohol hydrogenation were very similar [3]. Although 2-PhEt hydrogenation has not been studied over Pt, TOFs were obtained for hydrogenation of an isomer, 1-PhEt, on Pt/TiO₂ (LTR) and Pt/TiO₂ (HTR) [21]. If the TOFs for the isomers are assumed to be similar, comparison of the respective values at 373 K for 1-PhEt on Pt/TiO₂

(LTR) and Pt/TiO₂ (HTR), 0.085 and 0.060 s⁻¹, to the TOFs for PhAc on the same two respective catalysts, 0.014 and 0.026 s⁻¹, again indicates that very low surface coverages of PhEt must be responsible for the very low rates of formation of secondary products. The adsorption of PhAc compared to the intermediates formed is obviously favored, especially on Pt/TiO₂ (HTR).

Figs. 3–7 show that ring hydrogenated products such as cyclohexylethanal and cyclohexylethanol were usually produced in smaller concentrations and the total molar amount of hydrogenated carbonyl-bond-only products, i.e., styrene, 2-phenylethanol and ethylbenzene, increased with increasing conversion. These considerations plus the favored adsorption of PhAc on the catalysts show that PhAc hydrogenation to 2-PhEt rather than CyHxal is favored over all these Pt catalysts. The reduction of the C=O bond in PhAc was further enhanced at higher temperatures and higher conversions relative to the aromatic ring, thereby increasing the concentration of products created by C=O bond hydrogenation. Also, PhAc hydrogenation to CyHxal was significantly decreased over Pt/TiO₂ (HTR) at conversions ranging up to 60% and this behavior adds further support for the model invoking special interfacial sites which activate the carbonyl bond [13].

Metal crystallite size effects on activity and selectivity have been reported for the hydrogenation of several aldehydes and ketones, but no clear trends have been established because of contradictory results in the literature [11,22–27]. For example, Ru crystallite size had a profound effect on cinnamaldehyde hydrogenation in the liquid phase, with larger Ru particles showing a higher TOF [11]; however, Galvagno et al. reported a constant TOF for liquid-phase cinnamaldehyde hydrogenation over Ru/C catalysts with different dispersions [27]. Changes with particle size in the product distribution from cinnamaldehyde hydrogenation have been associated with steric effects which alter the distance between the surface and the aromatic

ring relative to the C=C bond because such steric constraints could not influence citral hydrogenation as the latter molecule contains no aromatic ring [27,28]. Differences were reported earlier for acetone hydrogenation over Pt powder and supported Pt [29] which have recently been attributed to the bonding geometry of C=O on the Pt surface [30]. The product distribution and specific activity for PhAc hydrogenation over 940 nm Pt powder particles were also different from those obtained with supported catalysts containing 1 nm Pt crystallites. At higher conversions, the TOF and the selectivity to ring-hydrogenated products like CyHxal and CyHxol were higher over Pt powder than over Pt/TiO₂ (HTR) and Pt/ η -Al₂O₃.

It is possible that the steady-state activities may be determined to a large extent by deactivation processes occurring during the initial minutes of the reaction. Deactivation of Pt catalysts by decarbonylation and subsequent irreversible CO adsorption possibly could occur during benzaldehyde and phenylacetaldehyde hydrogenation in a manner similar to that proposed by Englisch et al. for crotonaldehyde hydrogenation [22]. Deactivation and lower TOFs might be expected, therefore, to correlate inversely with toluene (and possibly benzene) formation and this is observed with the Pt/TiO₂ (HTR) catalyst. It is also known that the SMSI state existing in this catalyst weakens CO adsorption relative to H₂ adsorption [31], which could minimize this type of deactivation. However, it does not account for the higher activity that occurs with the Pt powder.

The extent of hydrogenolysis reactions (i.e. C–C bond breaking) decreased in the following order: Pt powder > Pt/SiO₂ > Pt/ η -Al₂O₃ > Pt/TiO₂ (LTR) > Pt/TiO₂ (HTR). This result is consistent with that obtained during benzaldehyde hydrogenation because hydrogenolysis was completely suppressed over Pt/TiO₂ (HTR) compared to the other catalysts [3]. It is usually assumed that hydrogenolysis of hydrocarbons requires large ensembles of metal atoms [32], and decoration of the metal surface by titania

Table 7
Specific activity for hydrogenation of aromatic oxygenates on Pt:
 $P_{\text{oxygenate}} = 3 \text{ Torr}$, $P_{\text{H}_2} = 750 \text{ Torr}$, $T = 423 \text{ K}$

Reactant	Turnover frequency ($\text{s}^{-1} \times 1000$) ^a		
	Pt/SiO ₂	Pt/ η -Al ₂ O ₃	Pt/TiO ₂ (HTR) ^b
Phenylacetaldehyde	24	31	652 (82)
Benzaldehyde ^c	48	69	1840 (176)
Acetophenone ^d	189	252	3240 (92)

^a Hydrogenolysis reactions excluded.

^b Value in parentheses based on Pt dispersion of unity.

^c From Ref. [3].

^d From Ref. [2].

can break up these ensembles thereby markedly affecting a structure-sensitive reaction such as this one [33]. This explanation readily accounts for the low hydrogenolysis rates obtained with the Pt/TiO₂ (HTR) catalyst.

A comparison of specific activity can now be made for the hydrogenation of three aromatic aldehydes and ketones over the same Pt catalysts. As shown in Table 7, the TOFs for benzaldehyde, phenylacetaldehyde, and acetophenone hydrogenation were always enhanced over Pt/TiO₂ (HTR) compared to typical Pt catalysts. Of the three compounds, PhAc was the least reactive with H₂, while acetophenone was the most reactive, regardless of catalyst. All three catalysts had average Pt crystallite sizes near 1 nm, thus eliminating crystallite size effects as a possible cause for the difference in activity. The activity enhancement over Pt/TiO₂ (HTR) for all three molecules can be explained by a single model which invokes special defect sites created at the Pt-titania interface which can polarize and activate the carbonyl bond [13]. A similar comparison for liquid-phase hydrogenation of acetophenone, cinnamaldehyde, and benzaldehyde over Ru catalysts has been made and the ketone was again reported to be much more reactive than the aldehydes [34]. These latter results and ours contrast to those of Jenck and Germain who found that alkyl aldehydes hydrogenated more rapidly than ketones over a copper chromite catalyst; however, they did state that the addition of a phenyl group to the neigh-

boring carbon atom activated the carbonyl group [19].

5. Summary

It has been found again that the product distribution in a hydrogenation reaction can be markedly altered by the appropriate choice of support material. Pt/TiO₂ (HTR) had a specific activity for PhAc hydrogenation that was, at a minimum, 2–5 times higher than the specific activities of Pt/SiO₂, Pt/ η -Al₂O₃ and Pt/TiO₂ (LTR). Hydrogenation of the C=O bond versus the aromatic ring was favored in this reaction over all the Pt catalysts. Perhaps more importantly, 2-PhAc formation was markedly enhanced over Pt/TiO₂ (HTR) giving selectivities near 70% even at conversions of 60%, which was double that of the best typical Pt catalyst, Pt/ η -Al₂O₃. In addition to enhanced activation of the carbonyl bond on Pt/TiO₂ (HTR) catalysts, desorption and readsorption processes, which control surface concentrations of the intermediates formed in the reaction, must also play a significant role in controlling secondary reactions and thus selectivity. Hydrogenolysis of PhAc to give toluene and, especially, benzene was more extensive on Pt powder at low conversions compared to the supported catalysts; however, at higher conversions of 60%, comparable hydrogenolysis activity (ca. half the product) occurred over all the catalysts except Pt/TiO₂ (HTR). Scission of C–C bonds was clearly suppressed on the HTR SMSI form of Pt/TiO₂ and this suppressed hydrogenolysis activity can be attributed to the destruction of large ensembles of Pt atoms by TiO_x species migrating onto the Pt surface. This type of activity enhancement coupled with improved selectivity to desired products continues to provide promise that MSI can be utilized to favorably impact both process economics and minimization of environmental waste associated with industrial hydrogenation reactions.

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