JOURNAL OF CATALYSIS **147**, 370–374 (1994)

NOTE

Metal-Support Effects on Intramolecular Selectivity during Acetophenone Hydrogenation over Pt Catalysts

The choice of support to disperse a metal can have a significant effect in certain reactions, and one of the best examples of metal–support interactions (MSI) is the hydrogenation of C=O bonds over noble metals such as Pt. It was first shown that the turnover frequency (TOF) for CH_4 formation on Pt from CO and H_2 could be increased by two orders of magnitude using TiO_2 as a support (1, 2). This reaction is structure insensitive and the TOF is independent of crystallite size (2, 3). The explanation we have preferred for this behavior is the creation of special sites at the metal–support interface which interact with the oxygen end of the molecule to enhance the reactivity of the C=O bond towards hydrogen (4, 5). As further support of this concept, the hydrogenation of acetone to isopropanol also showed marked enhancements in TOF (ca. 500-fold) over Pt/TiO_2 catalysts (6), and the intramolecular selectivity during crotonaldehyde hydrogenation was altered by favoring hydrogenation of the carbonyl bond compared to the C=C double bond to increase the crotyl alcohol/butyraldehyde product ratio (7). The next step in examining the influence of MSI on intramolecular selectivity was a comparison of the rates of hydrogenation of a carbonyl bond vs an aromatic ring, and acetophenone ($C_6H_5COCH_3$) represents one of the simplest molecules containing these two types of bond systems which also has a high enough vapor pressure to allow a vapor-phase reaction to be utilized. These results are reported here.

The supported platinum catalysts were those prepared, characterized, and described in a recent paper (8), and the metal dispersions given in Table 1 were determined by irreversible hydrogen adsorption (8). The pretreatments and reactor system have been described previously (8), but a 9-ft Carbowax 20M GC column was used for gas analysis. Acetophenone ((AcPh) Kodak, 99.7+%) was degassed by freeze–thaw cycles and stored under He. A bracketing technique using pure H_2 was used to minimize deactivation (6). The results described here were obtained at 10 Torr AcPh and 685 Torr H_2, and conversion was varied by altering space velocity at either 373 or 393 K. The reactor effluent was passed through an ice-water trap, and these condensates were analyzed by GC–mass spectroscopy. Thermal response factors had to be determined for a number of the reaction products, and these values, the procedure for obtaining them, and additional details about the reactor system are provided elsewhere (9). The reaction network associated with acetophenone (AcPh) hydrogenation can be very complicated, and in addition to the reactant, seven product compounds must be quantitatively identified—phenylethanol (PhEt), acetylcyclohexane (AcCy), 1-cyclohexylethanol (CyEt), ethylbenzene (EtBz), ethylcyclohexane (EtCy), styrene (Sty), and benzene (Bz)—to allow carbon mass balances to be obtained. Using a TR factor of 100 for benzene as the standard, the following TR factors were determined: AcPh, 132; PhEt, 135; AcCy, 140; CyEt, 169; EtBz, 125; EtCy, 134; and Sty, 121 (9). With these values, carbon balances within 10–15% were routinely obtained.

Conversions were sometimes quite high because of the high reactivity of these compounds and the need to operate at temperatures above the condensation temperatures to maintain a vapor-phase reaction. Some deactivation was usually observed and it was especially noticeable with the Pt/SiO_2 catalyst under the reaction conditions employed here thus preventing an accurate activation energy measurement. The kinetic properties of these catalysts are listed in Table 1.

Product selectivities determined using the space velocity to control conversion at either 373 or 393 K are shown in Figs. 1a–1e, in which the two sets of data are plotted together as they were indistinguishable within experimental uncertainty. Only small amounts of Sty were detected by GC–MS in the liquid condensate collected during these runs; EtBz was the principal product over the Pt/$SiO_2 \cdot Al_2O_3$ catalyst and PhEt was the major product with the Pt/TiO_2 catalyst, especially after the HTR treatment (10). These results were consistent with the GC analyses (9).

Only seven studies have described acetophenone hydrogenation over Pt (11–17), and none has contained rate data describing product formation. Turnover frequencies for AcPh hydrogenation at 358 K to all products are provided in Table 1, and TOFs for product formation based on the selectivities at 373 K are given in Table 2. However,

0021-9517/94 $6.00

TABLE 1

Acetophenone (AcPh) Hydrogenation over Pt Catalysts

Catalyst	T_{red} (K)	Disp. (H_{irr}/Pt_t)	r_0[a] (μmole/s/g cat)	E_A (kcal/mole)	Activity (at 358 K)	
					r (μmole/s/g cat)	TOF ($s^{-1} \times 10^3$)
0.96% Pt/SiO_2 I	723	0.96	[b]	[b]	3[b]	70[b]
0.78% Pt/Al_2O_3	723	1.03	4.0×10^6	10.0 ± 1.4	(0.11)[c]	(2)[c]
0.24% $Pt/SiO_2 \cdot Al_2O_3$	723	0.44	1.4×10^5	8.9 ± 4.0	3.23	78
0.95% Pt/TiO_2 (LTR)	473	0.73	2.8×10^3	5.1 ± 1.5	0.49	91
0.95% Pt/TiO_2 (HTR)	773	[0.02]	7.0×10^6	11.1 ± 1.8	2.33	66
					1.34	1300 (38)[d]

[a] r_0 is defined as $r = r_0 \cdot \exp(-E_A/RT)$.
[b] Initial activity.
[c] After severe deactivation.
[d] Turnover frequency based on the dispersion of LTR sample.

our primary objective was to determine if MSI could be used to alter selectivity in the hydrogenation of these two different bonds within a given molecule. Our previous investigations have established that TiO_2-supported metals have greatly increased TOFs for carbonyl bond hydrogenation (1–7), but the TOF for hydrogenation of aromatic molecules remains relatively unchanged (8, 18, 19) as do TOF values for the hydrogenation of other unsaturated C=C bonds (20, 21). Our model proposes the creation of special sites at the Pt–titania interface which can coordinate the oxygen end of the carbonyl bond and thus activate the C=O bond for hydrogenation (4); hydrogenation of unsaturated C=C bonds still occurs on the Pt surface and is little affected (8). This concept led to markedly enhanced selectivities to crotyl alcohol formation during crotonaldelyde hydrogenation (7), and in the simplest sense it can be viewed as a heterogeneous analogue to solvent effects reported for these reactions in the liquid phase (22).

TABLE 2

Specific Activities for Product Formation from Acetophenone (AcPh) Hydrogenation at 373 K[a], P_{AcPh} = 10 Torr, and P_{H_2} = 685 Torr

Catalyst	TOF ($s^{-1} \times 10^3$)					
	PhEt	EtBz	AcCy	CyEt	EtCy	Other
0.78% Pt/Al_2O_3	104	27	9	8	—	—
0.24% $Pt/SiO_2 \cdot Al_2O_3$	—	149	9	4	—	2
0.95% Pt/TiO_2 (LTR)	63	10	8	10	—	—
0.95% Pt/TiO_2 (HTR)	2400 (71)[b]	140 (4)[b]	—	73 (2)[b]		29 (1)[b]

[a] Based on the selectivities at 20% conversion reported in Figs. 1a–1e; see text for abbreviations.
[b] Based on the dispersion of the LTR sample.

As mentioned earlier, even a simplified reaction pathway is complex, and a comparison of free energy changes at 1 atm and 373 K calculated for the formation of AcCy, PhEt, EtBz, and Sty from AcPh shows that the formation of PhEt is not the thermodynamically favored route (10). Consequently, selectivity to PhEt must be controlled by reaction parameters such as rate constants and equilibrium adsorption constants. Platinum is not the best metal to test for MSI effects because it already possesses a reasonably high selectivity to PhEt which can be further enhanced by an appropriate choice of solvent during liquid-phase reactions (13–19). However, the use of Pt not only allows direct comparison with our previous studies with these same catalysts, but also provides an opportunity to look for analogies between solvent and support effects. Although a wide range of conversion was encountered in this study, there was no evidence of a decrease in apparent activation energies at higher rates, which implies that mass transfer limitations are not serious (9). The possibility of pore condensation of AcPh during the runs at lower temperatures was considered and calculations were made using the Kelvin equation (10); however, our results indicate that pore condensation did not have any significant effect on our kinetic data, and applications of the Weisz criterion (23) to these data also indicated that the rates were not affected by mass transport (9).

The activation energies for AcPh disappearance ranged from 5 to 11 kcal/mole, and these values encompass those reported for AcPh hydrogenation over Pt/SiO_2 (15) and $CuCr_2O_3$ (24) of 4.2 and 10.5 kcal/mole, respectively, and for PhEt and AcCy hydrogenation over Pt/SiO_2 of 4.0 and 10.3 kcal/mole, respectively (15). These low E_a values are also similar to those found for crotonaldehyde hydrogenation (7). Finally, E_a values for $Pt/SiO_2 \cdot Al_2O_3$ were obtained under differential reaction conditions at AcPh pres-

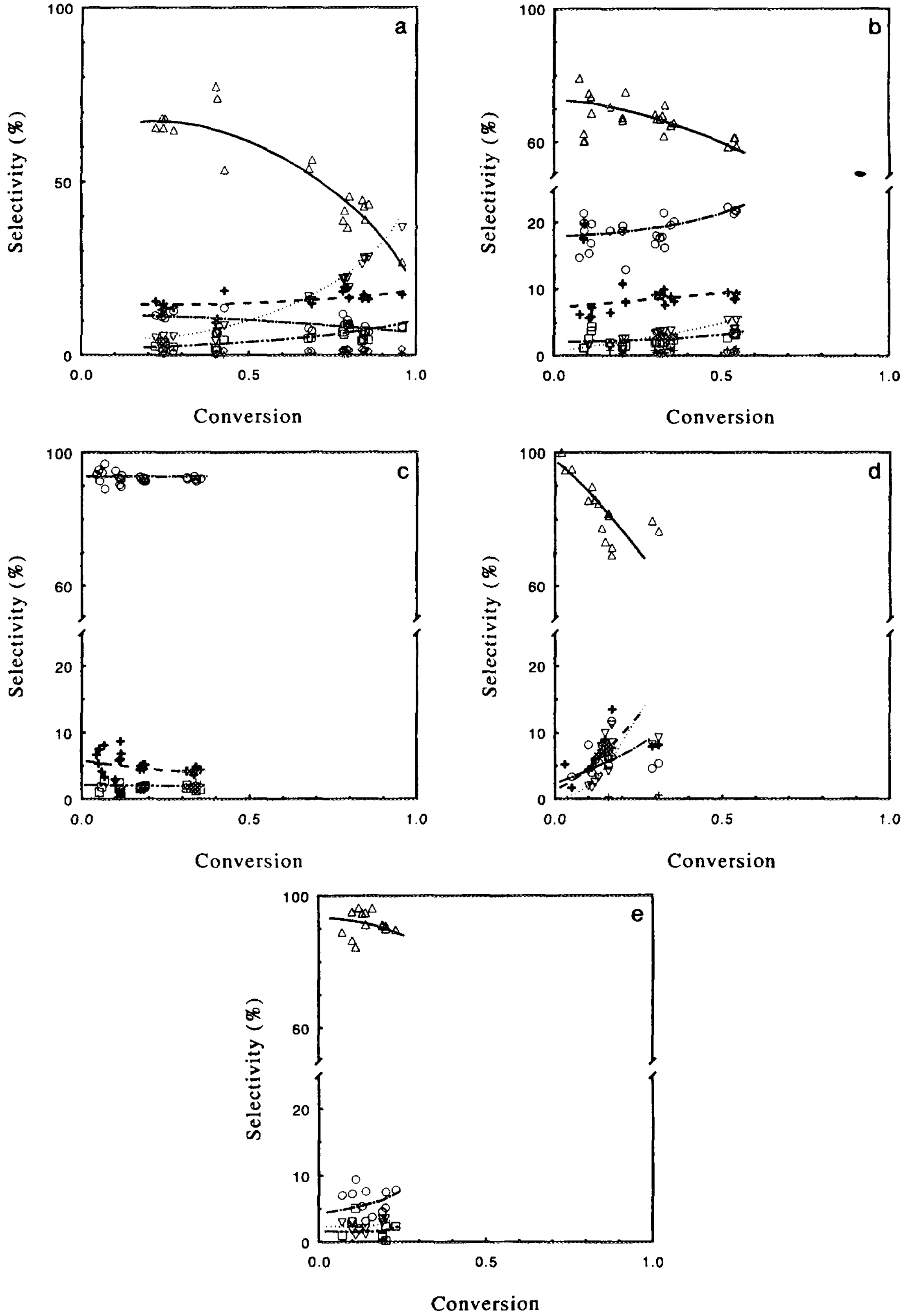

FIG. 1. Selectivity versus conversion for AcPh hydrogenation over Pt catalysts at P_{AcPh} = 10 Torr, P_{H_2} = 685 Torr, and 373 or 393 K: (a) 0.96% Pt/SiO_2, (b) 0.78% Pt/Al_2O_3, (c) 0.24% $Pt/SiO_2 \cdot Al_2O_3$, (d) 0.95% Pt/TiO_2 (LTR), and (e) 0.95% Pt/TiO_2 (HTR). PhEt (△); EtBz (○); AcCy (+); CyEt (▽); EtCy (+); Bz (◇); the decomposition product from CyEt (□). Conversions were controlled by space velocity. Note the expanded lower scale in (b–e).

sures of both 3 and 10 Torr, and both values were nearly identical and close to 9 kcal/mole (9); therefore, it appears that these E_a values are intrinsic to this type of reaction and do not necessarily represent diffusional limitations. Of course, large variations in product distribution could affect these values. If the initial activity of Pt/SiO_2, which exhibited severe deactivation, is considered, the TOF values do not vary widely as different supports are used; for example, at 358 K the range is 0.066 to 0.091 s^{-1} for the typical catalysts and the TOF is 0.038 s^{-1} for the Pt/TiO_2 (HTR) catalyst if the Pt surface area is assumed to remain constant in the LTR and HTR Pt/TiO_2 catalysts. If, however, sites are counted by hydrogen adsorption at 300 K, much higher TOF values are obtained because of the reduced chemisorption capacity; regardless, the latter measurement should give the minimum number of adsorption sites as H_2 must be activated. During liquid-phase hydrogenation over Pt catalysts, near zero-order rate dependencies on AcPh have been reported (17–19) and, under differential reaction conditions, the $Pt/SiO_2 \cdot Al_2O_3$ catalyst had a reaction order on AcPh of 0.3 (9).

Except for $Pt/SiO_2 \cdot Al_2O_3$, selectivities to PhEt were routinely above 50%, as shown in Fig. 1, until AcPh conversions greater than 80% were attained, at which point this selectivity could drop noticeably (Fig. 1a). With $Pt/SiO_2 \cdot Al_2O_3$ selectivities to EtBz of over 95% were obtained, as indicated in Fig. 1c, but this behavior is consistent with the increase in EtBz formation which has been obtained upon the addition of Brønsted or Lewis acids to liquid-phase reactions (25, 26). This acidic $SiO_2 \cdot Al_2O_3$ support provides a bifunctional route for EtBz formation, i.e., production of PhEt on the Pt, dehydration of PhEt to styrene on acid sites on the support, then adsorption of Sty on the Pt followed by hydrogenation to EtBz. This pathway is further verified by the study of Takahashi *et al.*, which demonstrated that PhEt dehydrates to Sty over solid acid catalysts in the absence of H_2 (27).

For Pt dispersed on supports with low acidity, selectivity to PhEt was clearly enhanced by the use of TiO_2, particularly after a HTR pretreatment. Maximum selectivities to PhEt over Pt/SiO_2 and Pt/Al_2O_3 were approximately 70 to 80% at low conversion (Figs. 1a, 1b); however, this selectivity can decrease significantly at high conversions, as shown in Fig. 1a. Over Pt/SiO_2, AcCy was the second most predominant product (ca. 15%), followed by EtBz (ca. 12%), until high conversions were reached and CyEt became the major product (Fig. 1a). The largest difference over Pt/Al_2O_3 was a switch in the relative amounts of AcCy and EtBz, as about 20% of the product was comprised of the latter compound (Fig. 1b). Both Pt/TiO_2 catalysts showed a marked increase in PhEt selectivity, but the LTR catalyst exhibited a decrease in selectivity as conversion increased, and the selectivity dropped from about 100% at low conversions to near 70% at higher conversions as the amounts of CyEt and AcCy increased (Fig. 1d). The Pt/TiO_2 (HTR) catalyst, however, retained a selectivity of 85% or higher up to conversions of 20% (Fig. 1e), and it remained close to 80% even at conversions above 70% (9). The only other significant products were EtBz and CyEt. Thus, there is an unequivocal enhancement in selectivity to PhEt when TiO_2 is used, although specific activities remained similar on these four catalysts, thus indicating a change in the type of site capable of adding the first two H atoms to the carbonyl bond.

These results indicate that a large variation in product distribution can be caused by the support. From activities at 373 K taken from Arrhenius plots (9), TOF values can be calculated for the rates of formation of the different products, and they are shown in Table 2. However, it must be remembered that these are rates that typically exist with AcPh as the primary vapor-phase species. As mentioned previously, in liquid-phase reactions both the solvent and additives to the solvent have been shown to have a significant effect on activity and selectivity (11–13, 15, 17, 25, 26). To some extent, then, the MSI effects in this reaction could be viewed as a heterogeneous analogue to solvent effects reported for this reaction in the liquid phase.

The retention of high selectivity to PhEt over these catalysts (with the exception of $Pt/SiO_2 \cdot Al_2O_3$) at high conversions, i.e., at high concentrations of PhEt and lower concentrations of AcPh, implies a strong effect due to competitive chemisorption because hydrogenation rates of PhEt and AcCy are comparable to or greater than that for AcPh when either of the former molecules is used as a pure reactant (15, 28). A previous study by van Bekkum *et al.* of competitive hydrogenation of AcPh/AcCy mixtures has demonstated such an adsorption effect (29), and in a PhEt/AcCy mixture the former is also preferentially hydrogenated over Rh (30). These results indicate more favorable adsorption associated with the aromatic ring compared to a saturated cycloparaffin. Regardless, this factor alone cannot account for the rate enhancement of PhEt formation relative to AcCy formation over Pt/TiO_2 (HTR), especially when compared to Pt/SiO_2, because AcCy is almost completely suppressed over the Pt/TiO_2 (HTR) catalyst. We forward this behavior as additional evidence in support of our model of interfacial active sites existing in Pt/TiO_2 systems which can selectively activate carbonyl bonds (4, 5). As benzene and other aromatic molecules are typically π-bonded on a metal surface in the absence of steric hindrance (31, 32), this coordination is assumed to remain, but an additional interaction occurs between the oxygen in the side-chain carbonyl group and a defect site on the titania surface, such as an oxygen vacancy. Such a bonding mode for the carbonyl group in AcPh was proposed on Rh–Sn catalysts by Zakumbaeva *et al.* based on IR spectra (33); this would polarize the bond and activate it towards hydrogen. A very recent paper by Aramendia *et al.* has shown an inverse linear relationship between the specific activity of AcPh hydrogenation on Pd and the dielectric constant of the solvent; however, this effect was explained by a solvating effect of AcPh that hinders its adsorption on the metal (34).

ACKNOWLEDGMENT

This study was supported by the U.S. Department of Energy, Division of Basic Energy Sciences, under Grant DE-FG02-84ER13276.

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Received September 27, 1993; revised December 13, 1993