JOURNAL OF CATALYSIS **147**, 375–378 (1994)

NOTE

Hydrogenation of Phenylethanol and Acetylcyclohexane over Pt

The control of intramolecular selectivity when both unsaturated C=C bonds and carbonyl groups are present is of commercial importance. Group VIII metals, particularly Ni and Pt, are used to hydrogenate aromatic hydrocarbons, and copper chromite catalysts have routinely been used to hydrogenate carbonyl groups in aromatic molecules as they are relatively inactive for hydrogenating aromatic rings (1). We have recently studied acetophenone ($C_6H_5COCH_3$) hydrogenation over Pt to determine the relative rates of phenylethanol ($C_6H_5CHOHCH_3$) formation versus acetylcyclohexane ($C_6H_{11}COCH_3$) formation and to examine the influence of the support on product selectivity (2, 3). Phenylethanol constituted about 60–70 mole% of the product over typical Pt catalysts such as Pt/SiO_2 and $Pt/\eta\text{-}Al_2O_3$, even at conversions up to 50%; however, the use of TiO_2 as a support shifted the selectivity to 90% or higher (2, 3). There are numerous products possible in this reaction network, and two major considerations exist to account for the high selectivity to PhEt, especially at high acetophenone conversions—the intrinsic hydrogenation rates of the various compounds or their relative surface coverages under reaction conditions, i.e., competitive adsorption. To see which of these two factors is predominant in this reaction system, the vapor-phase hydrogenation of phenylethanol (PhEt) and acetylcyclohexane (AcCy) was studied over Pt and compared to acetophenone (AcPh) hydrogenation rates. Neither PhEt nor AcCy hydrogenation over Pt has been studied; consequently, the first specific activities of these reactions are reported here.

The catalysts, reactor system, pretreatments, and GC analysis procedure are given elsewhere (2, 3). The Pt/TiO_2 catalysts were given either a low-temperature reduction (LTR) at 473 K which resulted in normal H_2 chemisorption, or a high-temperature reduction (HTR) at 773 K which induced suppressed chemisorption, while the $Pt/\eta\text{-}Al_2O_3$ catalyst was reduced at 723 K. The dispersions of 0.95% Pt/TiO_2 (LTR) and 0.78% $Pt/\eta\text{-}Al_2O_3$ were 0.73 and 0.96, respectively, based on irreversible H chemisorption. Each reactant—AcPh (Kodak, 99.7+%), PhEt (Fluka Chemie, 98+%), and AcCy (Fluka AG, 95%)—was degassed by repeated freeze—thaw cycles under flowing He (MG Ind., 99.999%) and stored under He in a reservoir connected to a Sage syringe pump via a three-way valve to allow refilling without air exposure. The reactant was then pumped at a rate to give either 5 or 10 Torr partial pressure in 685 Torr H_2 (MG Ind., 99.999+%) with the balance being He. Gas chromatographic analyses were conducted using a H-P 5890 GC equipped with a thermal conductivity detector and a 9-ft Carbowax 20M column. Thermal response factors were determined for these reactants and the possible products (3). Rates were measured at temperatures near 373 K, and reactions were typically run for 1–2 h on stream under a given set of reaction conditions to observe activity maintenance. A series of 4–7 such runs was conducted with each catalyst; thus the long-term activity after a total of 8–15 h on stream could be obtained. With the exception of the Pt/TiO_2 (HTR) catalyst, significant deactivation was observed.

Figure 1 shows PhEt activity versus total time on stream for the 0.95% Pt/TiO_2 (HTR) catalyst. No results are shown from 200 to 300 min because of erratic GC performance. Here the conversion initially increases from below 20% to line out at about 25%. In contrast, the worst case of deactivation was with AcCy hydrogenation over 0.78% $Pt/\eta\text{-}Al_2O_3$, which never stabilized, and the conversion decreased continuously with time on stream from near 70% to about 10% as shown in Fig. 2. Initial activities were estimated by taking the average of the activities measured during the first 50 min on stream, with the exception of PhEt hydrogenation over Pt/TiO_2 (HTR) for which the higher, stabilized activity was used. These values along with turnover frequencies (TOFs) based on Pt dispersion are listed in Table 1. Selectivities and TOFs for the formation of various products during PhEt hydrogenation over the two Pt/TiO_2 catalysts are given in Table 2, while similar information about AcCy hydrogenation over $Pt/\eta\text{-}Al_2O_3$ is provided in Table 3. These results are average values obtained from 4–5 runs conducted at reactant conversions near 20% to allow comparison with results for AcPh hydrogenation over these same catalysts which are given elsewhere (2, 3).

Analyses by gas chromatography were complicated by the decomposition of PhEt in both the stainless steel effluent line to the gas sampling valve and the valve itself, both of which were heated to prevent condensation. A

0021-9517/94 $6.00

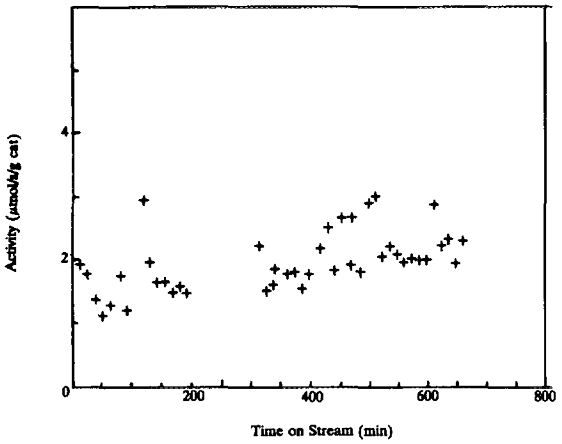

FIG. 1. Phenylethanol (PhEt) hydrogenation activity over 0.95% Pt/TiO_2 (HTR) versus total time on stream. T = 373 K; P_{PhEt} = 10 Torr; P_{H_2} = 685 Torr; balance, He.

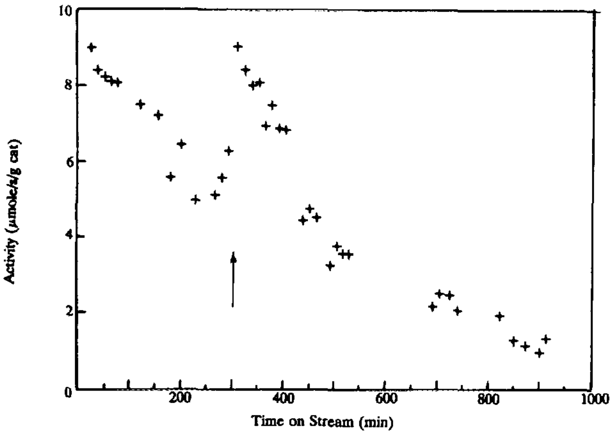

FIG. 2. Acetylcyclohexane (AcCy) hydrogenation activity over 0.78% Pt/η-Al_2O_3 versus total time on stream. T = 370–395 K, P_{AcCy} = 5 Torr, P_{H_2} = 685 Torr, Balance He. Catalyst was regenerated in H_2 after 300 min on stream (arrow).

PhEt/He mixture passed through an empty reactor at 373 K produced a decomposition product peak with the same retention time and thermal response factor as styrene, and GC–MS analysis confirmed the presence of styrene. Assuming this was the product, the average conversion to styrene was 21%. With either pure TiO_2 (LTR) or TiO_2 (HTR) in the reactor, conversions increased somewhat to about 25%. Consequently, all analyses involving styrene formation were reduced by 21% to correct as well as possible for this background PhEt decomposition reaction.

Hydrogenation reactions of organic compounds similar to those represented by acetophenone (AcPh), phenylethanol (PhEt), and acetylcyclohexane (AcCy) are likely to be encountered in the production of fine chemicals and specialty intermediates. In our earlier study of acetophenone hydrogenation over Pt, the influence of the support on intramolecular selectivity was examined, and the use of TiO_2 as a support significantly enhanced the selectivity to PhEt (2, 3). At low conversions, nearly all the product was PhEt over the Pt/TiO_2 catalysts compared to 70–80% for Pt/SiO_2 and Pt/Al_2O_3, and even at conversions near 70% over the (HTR) Pt/TiO_2 catalyst, the selectivity to PhEt remained near 80% compared to less than 50% over Pt/SiO_2 (2, 3). There are two principal ways to explain how this high selectivity to PhEt is maintained at high AcPh conversions when AcCy and PhEt concentrations, particularly the latter, can become large, in other words, to explain why secondary reactions to CyEt and EtBz are suppressed. The first is that the intrinsic hydrogenation rate of AcPh compared to AcCy and PhEt is much higher, which would give much higher rates even if comparable surface coverages existed. The second is that a much more preferable adsorption of AcPh results in selective chemisorption and much higher relative surface coverages of AcPh, which would result in much higher rates even if intrinsic reactivities were similar. We were interested

TABLE 1

Initial Hydrogenation Activity over Pt Catalysts (T = 373 K, P_{H_2} = 685 Torr)

Reactant	Catalyst	P (Torr)	Activity	
			μmole/s/g cat	TOF (s^{-1})
Acetophenone (AcPh)	0.95% Pt/TiO_2 (LTR)	10	4.0	0.11
	0.95% Pt/TiO_2 (HTR)	10	3.1	0.088[a]
	0.78% Pt/η-Al_2O_3	~5	4[b]	0.1[b]
Phenylethanol (PhEt)	0.95% Pt/TiO_2 (LTR)	10	3.0	0.085
	0.95% Pt/TiO_2 (HTR)	10	2.1	0.060[a]
Acetylcyclohexane (AcCy)	0.78% Pt/η-Al_2O_3	5	8.4	0.21

[a] Assuming Pt dispersion is identical to the 0.95% Pt/TiO_2 (LTR) catalyst.

[b] Estimated from Ref. (2).

TABLE 2

Product Selectivity and Rates of Formation during Phenylethanol (PhEt) Hydrogenation over 0.95% Pt/TiO$_2$ (T ≅ 373 K, P_{PhEt} = 10 Torr, P_{H_2} = 685 Torr)

Product	LTR (Conv. = 18%) Mole%	LTR (Conv. = 18%) TOF (s^{-1})	HTR (Conv. = 19%) Mole%	HTR (Conv. = 19%) TOF (s^{-1})	Rh/Al$_2$O$_3$[a] (28% Conv.) Mole%
Styrene (Sty)	32	0.027	27	0.016	—
Cyclohexylethanol (CyEt)	33	0.028	34	0.021	59.6
Ethylbenzene (EtBz)	21	0.018	32	0.019	26.1
Acetylcyclohexane (AcCy)	8	0.006	1	0.001	14.3
Acetophenone (AcPh)	4	0.003	3	0.002	—
Ethylcyclohexane (EtCy)	3	0.002	2	0.001	—

[a] From Ref. (4) P_{H_2} = 80 atm; T = 353 K; solvent, C$_2$H$_5$OH.

in determining which possibility is dominant. These explanations apply to typical sites on the Pt surface as well as interfacial sites which enhance PhEt formation (2, 3).

Turnover frequencies (TOFs) for AcPh disappearance as well as PhEt and AcCy formation from AcPh were recently determined and reported because no specific activities had been previously measured (2, 3). A similar situation exists with regard to rates of PhEt and AcCy hydrogenation, as they have not been measured over Pt and only one study has examined these reactions over any catalyst, Rh/Al$_2$O$_3$ in this case, but no specific activities were reported (4). The initial rates of hydrogenation of the pure reactants are given in Table 1. The specific activities for AcPh over the two 0.95% Pt/TiO$_2$ catalysts are in good agreement with the results obtained previously (2, 3). Of principal importance is the similarity of TOF values for hydrogenation of these three molecules under comparable conditions, i.e., when each is the lone organic reactant in the feed. Initial TOFs for AcPh are similar over (LTR) and (HTR) Pt/TiO$_2$, but the latter exhibits much better activity maintenance. The TOFs for PhEt hydrogenation are only about 25–30% lower than those for AcPh on the same catalyst, while the TOF for AcCy is approximately twice as large as that for AcPh on either Pt/TiO$_2$ or Pt/η-Al$_2$O$_3$. No adsorption data for these molecules on any metal surface could be found; however, based on these relative reaction rates it is clear that low surface concentrations on Pt must be the reason that PhEt and AcCy, when present, have low hydrogenation rates in the presence of AcPh (2, 3). In other words, as long as the concentration of AcPh is high enouth, selective adsorption of this aromatic compound is predominant and only very low surface concentrations of the partially hydrogenated intermediates exist. Additional verification of this situation has been nicely demonstrated recently by Aramendia *et al.* during AcPh hydrogenation over Pd to ethylbenzene via PhEt as the intermediate (5). This finding does not pertain to the initial selectivity between PhEt and AcCy (steps 1 and 2, Fig. 3), but it does account for the high selectivities to PhEt that are maintained at higher conversions (2, 3).

TABLE 3

Selectivity and Rates of Formation during Acetycyclohexane (AcCy) Hydrogenation over Pt/η-Al$_2$O$_3$ (T = 370–396 K, P_{AcCy} = 5 Torr, P_{H_2} = 685 Torr)

Product	Conv. (%)	Mole%	TOF (s^{-1})	Rh/Al$_2$O$_3$[a] Mole% (95.6% Conv.)
Cyclohexylethanol	20	90	0.19	30.9
(CyEt)	70	94	—	
Ethylcyclohexane	20	5	0.01	2.5
(EtCy)	70	4	—	
Ethylbenzene	20	5	0.01	13.8
(EtBz)	70	2	—	
Phenylethanol (PhEt)	—	—	—	52.8

[a] From Ref. (4), P_{H_2} = 80 atm; T = 353 K; solvent, C$_2$H$_5$OH.

The principal possible products in this system are shown in Fig. 3, which demonstrates that the reaction network can be rather complex. With PhEt as the only organic reactant, about one-third of the product was cyclohexylethanol (CyEt), and the sum of styrene (Sty)

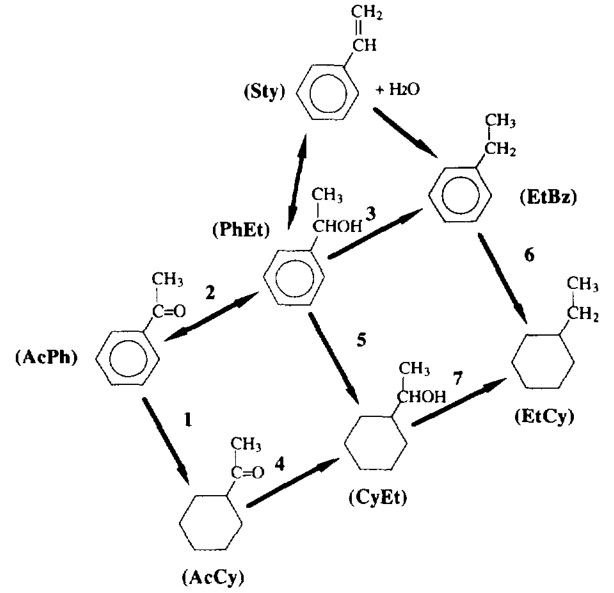

FIG. 3. Reaction network for hydrogenation of phenylethanol (PhEt) and acetylcyclohexane (AcCy). Arrows indicate favorable reaction directions based on free energy changes at 373 K.

plus ethylbenzene (EtBz) constituted 50–60% of the product over either the (LTR) or the (HTR) Pt/TiO_2 catalyst, with the Sty/EtBz ratio being higher over the former sample. Thermodynamic calculations indicate that the standard free energies of reaction at 298 K are negative for the formation of all compounds from PhEt except AcPh (+5.9 kcal/mole) and Sty (+1.9 kca/mole), but at 373 K ΔG°_R for styrene also becomes negative (−1.2 kcal/mole) although ΔG°_R remains positive (+4.2 kcal/mole) for AcPh (6). Consequently, at 373 K the low AcPh levels may be controlled by equilibrium, whereas the styrene concentrations are within the limits allowed by thermodynamics and are determined by kinetics. The three principal products—CyEt, Sty, and EtBz—can all be formed directly from PhEt, with Sty most likely bring formed via a dehydration reaction on acid sites on the support surface (2, 3). This consideration plus the small amounts of other compounds, especially over the (HTR) Pt/TiO_2 catalyst, strongly implies that PhEt is the predominant adsorbed reactant in this reaction network, and in the absence of significant concentrations of AcPh, its specific activity is comparable to that of AcPh.

When AcCy is the only organic in the feed, the reaction is much cleaner as only one primary product can be formed (Fig. 3), and 90% of the product is CyEt with equal amounts of EtCy and EtBz comprising the balance at low conversions. At high conversions, the selectivity shifts even more towards CyEt. This implies either that the relative surface concentration of AcCy, with its carbonyl bond, is much higher than any other species or that the primary product, CyEt, has a very low hydrogenation rate. Perhaps the greatest surprise is the amount of EtBz that is detected. However, in the absence of AcPh and at very low concentrations of any other aromatic compounds, the TOF for the hydrogenation of AcCy is twice that of AcPh; thus the retention of significant amounts of AcCy in the product during AcPh hydrogenation over Pt, as observed for the Pt/SiO_2 catalyst (2, 3), must be due to its very low surface concentration under reaction conditions. All of these results clearly indicate that AcPh must be the most abundant surface species on all active sites when it is being hydrogenated over dispersed Pd catalysts.

In summary, when present as the only reactant in the feed, the hydrogenation rate of phenylethanol is only about 25% lower than that of acetophenone, while the turnover frequency for acetylcyclohexane hydrogenation is double that for acetophenone. AcCy hydrogenation gives a very high selectivity of over 90% to CyEt, thus demonstrating a similar situation with these cyclic paraffinic organic compounds; i.e., the surface retains a relative high coverage of AcCy, which has a carbonyl group, even up to high conversions, and coverages of the intermediate products are very low. With PhEt hydrogenation, three products—CyEt, Styrene, and EtBz—are made in comparable quantities of 20–35% each, thus indicating that Sty can compete successfully with PhEt for adsorption sites on the Pt surface. This study demonstrates that the high initial selectivities to phenylethanol during acetophenone hydrogenation over Pt catalysts, especially Pt/TiO_2, are maintained at high conversions because of selective AcPh chemisorption rather than intrinsically low reaction rates of the intermediate compounds with adsorbed hydrogen.

ACKNOWLEDGMENT

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

REFERENCES

1. Thomas, C. L., "Catalytic Processes and Proven Catalysts," Academic Press, New York, 1970.
2. Lin, S. D., Sanders, D. K., and Vannice, M. A., *J. Catal.* **147,** 370 (1994).
3. Lin, S. D., Sanders, D. K., and Vannice, M. A., *Appl. Catal.*, In press.
4. Friedlin, L. Kh., Borunova, N. V., Gvinter, L. I., Danielova, S. S., and Badakh, R. N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1797 (1970).
5. Aramendia, M. A., Borau, V., Gomez, J. F., Herrera, A., Jimenez, C. and Marinas, J. M., *J. Catal.* **140,** 335 (1993).
6. Lin, S. D., Ph.D. thesis, The Pennsylvania State University, 1992.

Diane K. Sanders
S.-D. Lin
M. A. Vannice

Department of Chemical Engineering
The Pennsylvania State University
University Park, Pennsylvania 16802

Received October 22, 1993; revised January 3, 1994