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Heterogeneously Catalyzed Vapor-Phase Oxidation of Ethylene to Acetaldehyde

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A heterogeneous catalyst system has been developed for the vapor-phase oxidation of ethylene to acetaldehyde. The catalyst consists of palladium-doped vanadium pentoxide and, usually, a third component such as Ti, Ru, Pt, or Ir. Mechanistic studies, especially by ESR spectroscopy, have established a redox mechanism with the palladium ions playing a central role. The catalyst system operates under mild conditions (110–175°C and 1–30 atm) with good efficiency and high space–time yields.

INTRODUCTION

The discovery in 1959 by Smidt *et al.* (*1*), that acetaldehyde could be prepared catalytically and efficiently in one step from ethylene using a homogeneous system containing $PdCl_2 + CuCl_2$ has had important ramifications. The Wacker process, which is based on this discovery, has become the major industrial route to acetaldehyde (*2*) and the success of the process has inspired much basic research in homogeneous and heterogeneous catalysis.

In marked contrast to the recent experience with industrially important catalytic reactions (*3*), no heterogeneously catalyzed analog of the Wacker reaction has been developed. A search of the literature does reveal references to the vapor-phase, catalytic oxidation of ethylene to acetaldehyde (*4*), acetic acid (*5*) or both (*6*), but none appears to have been successfully developed. A close examination of most of this work suggests that catalyst systems used, to date, either lacked sufficient activity or stability. Problems with catalyst lifetime appear to be particularly pronounced for heterogeneous systems closely resembling the $PdCl_2 + CuCl_2$ solution catalyst (*7*). The role of the $CuCl_2$ in the Wacker process is to oxidize Pd(0) to Pd(II); it is much more difficult for the Cu^{II} to accomplish this when supported on a surface since there are problems with the proximity of Cu^{II} and Pd ions and with rapid reoxidation of the Cu^{I}.

In order to develop a solid catalyst which could function similarly to the Wacker-type solution catalyst it appeared to be necessary to combine the palladium with a solid which was capable of reoxidizing Pd^0 to Pd^{2+} with great efficiency. This paper describes our work on the development of a Pd-containing solid which is capable of oxidizing ethylene in the vapor phase directly to acetaldehyde with high specificity, activity and stability.

RESULTS

Catalyst Development

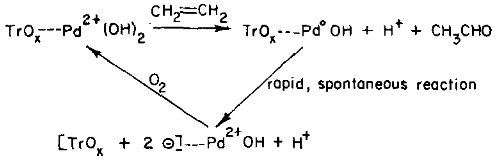
In the design of a solid catalyst for the oxidation of ethylene to acetaldehyde we assumed that a noble metal, probably palladium would be required to perform the ligand specific function involving insertion of the olefin into a metal–OH bond and its ultimate conversion to acetaldehyde. The reoxidation by air of the Pd^0, obtained in the formation of a molecule of acetaldehyde, is too slow under the conditions of this reaction. Accordingly, the palladium had to be linked to a cocatalyst which could catalyze its reoxidation to Pd^{2+}, and which in turn could be oxidized by oxygen via electron transfer at the noble metal site. It further appeared necessary that

a. the Pd^{2+} should be linked directly to the cocatalyst as a surface complex;

b. the cocatalyst should be substantially inert to ethylene and acetaldehyde under the conditions of reaction, i.e., it must not be reduced by the reactants in the absence of Pd^{2+};

c. the cocatalyst should be capable of oxidizing the same Pd^0 atom many times before itself becomes reoxidized.

The simple model for the mechanism considered at this point was as follows:



The requirements for the catalyst pointed to a transition metal oxide containing a cation of high valence. It also had to be a semiconductor in order to transfer the electrons rapidly and to accept several electrons without reoxidation. The latter was considered especially important for catalyst stability because the palladium reoxidized by the cocatalyst might, on occasion, react with a second molecule of ethylene before the cocatalyst was oxidized. Ideally, the cocatalyst should receive or donate electrons as a single semiconductor unit to every palladium on its crystal surface depending on its ligand, ethylene or oxygen, respectively. A final consideration, that directed our attention towards oxides was the requirement of structural stability during the redox process. It was felt that these requirements will be best met by a transition metal oxide rather than by a salt not only because the requirement for good conductivity but also because of the need for structural stability during the redox process.

Of all transition metal oxides tested, however, only vanadium pentoxide and certain vanadium oxide containing mixed oxides were found to be capable of performing as effective cocatalysts with palladium. Catalysts containing 3–15 wt % vanadium pentoxide and 0.01–1.0 wt % palladium were capable to convert ethylene to acetaldehyde, with acetic acid as by-product, already at 110°C with excellent selectivity and productivity:

$$CH_2{=}CH_2 + O_2 + H_2O \xrightarrow[\text{Pd–X–}V_2O_5]{\substack{110\text{–}185°C \\ 1\text{–}30\ \text{atm}}}$$

$$(X = \text{Ti, Ru, Ir, Pt})\ \underset{60\text{–}85\%}{CH_3CHO} + \underset{25\text{–}10\%}{CH_3CO_2H}$$

All Pd-transition metal oxide systems not containing vanadium were inert or showed only marginal catalytic effects. Inert compositions included Pd–Co_2O_3, Pd–CuO, Pd–MoO_3, Pd–WO_3. Very little or no activity was observed when the Pd was substituted by other noble metals in the vanadium pentoxide based system: Ru–V_2O_5 and Pt–V_2O_5 systems were inactive. The combination of Pd salts with $CuCl_2$ or other transition metal salts resulted in catalysts with some initial activity but with very short lives. Examination of the used salt-type catalysts revealed that the palladium was in the metal state (Pd^0) indicating these salts lacked the ability to maintain a stable complex with the palladium during the redox process, see Tables 1 and 2.

The relationship between the palladium and the vanadium oxide is synergistic since neither of the components is active alone, for a significant period of time, for the oxidation of ethylene. The combination of the two, affords a catalyst of very high productivity, see Table 2 (*8*). Furthermore, these catalysts are relatively stable.

Catalysts containing Pd, Ru and V_2O_5 on α-Al_2O_3 have been run continuously for periods up to 5 weeks under the conditions of Table 1. Their stability is orders of magnitude better than that of mixtures of palladium salts and transition metal salts or of palladium oxide (Fig. 1). At very high space velocities and temperatures of approximately 170°C (>3 mol/liter cat/hr C_2H_4 conv.), a slow decline in activity was observed during extended use but occasional

TABLE 1
OXIDATION OF ETHYLENE AT 1 atm[a]

Catalyst comp.[b] (wt %)	T (°C)	C_2H_4 conv. (%)	Efficiencies	
			$CH_3\overset{\overset{O}{\|}}{C}H$ (%)	CH_3CO_2H (%)
		Ethylene		
V_2O_5(17)	140	4	Tr	~20
Pd(0.8)[c]	140	~9	Tr	
Ru(0.8)-V_2O_5(17)	140	1	Tr	
Pd(0.8)-CuO(17)	140	4	Tr	~25
Pd(0.8)-V_2O_5(17)	140	72	70	18
Pd(0.8)-Ru(0.4)-V_2O_5(17)	140	90	64	20
Pd(0.8)-Ir(1.5)-V_2O_5(17)	122	70	70	20
Pd(0.8)-Rh(0.8)-V_2O_5(17)	140	50	63	25
Pd(0.8)-Cu(0.8)-V_2O_5(17)	140	65	68	24

[a] In a 1 in. i.d. glass, tubular reactor; the gas hourly space velocity (GHSV) was 200 and the feed was C_2H_4 (4%), O_2 (15%), H_2O (28%) and N_2 (53%).

[b] Supported on α-Al_2O_3.

[c] Rapidly lost activity.

reactivation with oxygen or air at $T >$ 300°C restored activity.

Catalyst Studies

A preliminary survey of the electron spin resonance spectra of Pd–V_2O_5–alumina catalysts revealed the existence of a broad resonance signal near the $g = 2.0$ region. The same signal was observed at room temperature as well as at liquid nitrogen temperature. The signal was observed with V_2O_5–alumina but not with PdO–alumina,

TABLE 2
OXIDATIONS OF ETHYLENE AT ELEVATED PRESSURES

Catalyst[a] (wt %)	C_2H_5 conv. (%)	Efficiencies	
		$CH_3\overset{\overset{O}{\|}}{C}H$	CH_3CO_2H
a. Ethylene oxidation at 146°, 115 psia[b]			
Pd(0.4)-Ti(0.4)-V_2O_5(17)	36	75	14.5
Pd(0.4)-Ti(4.0)-V_2O_5(10)	36	75.5	14
Pd(0.8)-V_2O_5(17)	29	65	25
Pd(0.4)-V_2O_5(17)[c]	21	79.5	12.4
Pd(0.4)-Cr(0.4)-V_2O_5(17)[d]	29	83	9.6
Pd(0.01)-V_2O_5(5)[c]	23	81	10.5
b. Ethylene oxidation at 170° and 115 psia in recirculating back-mixed reactor[e]			
Pd(0.1)-Ti(0.4)-V_2O_5(17)[c]	40	69.7	17.1

[a] Catalysts were supported on α-Al_2O_3.

[b] In 1 in. i.d., tubular, stainless steel reactor; GHSV ~1650. The feed was C_2H_5 (3.6%), O_2 (9.5%), H_2O (11%) and N_2 (76%).

[c] Prepared via palladium polyvanadate.

[d] Prepared via palladium chromate.

[e] Feed: C_2H_4 (3.8%), O_2 (9.5%), H_2O (11%), N_2 (74%).

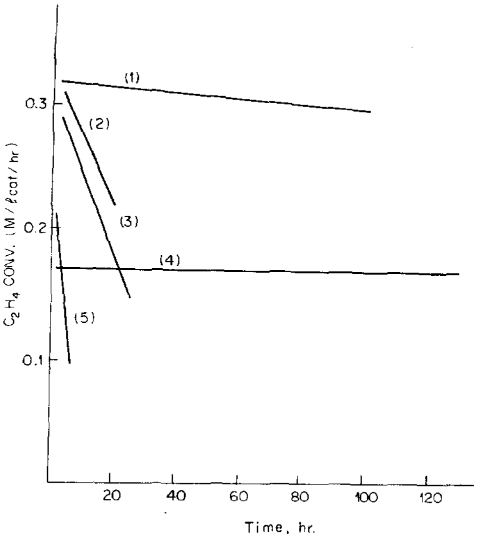


FIG. 1. Stability of various catalysts for C_2H_4 oxidation; utilizing the conditions described in Table 1. Catalysts: (1) Pd^{2+} (0.8%)–Ru^{3+} (0.4%)–V_2O_5 (17%); (2) Pd^0 (0.8%)–V_2O_5 (17%); (3) $PdCl_2$–$CuCl_2$–$FeCl_3$–V_2O_5 (1.0%); not activated at high temp to eliminate Cl^-; (4) Pd^{2+} (0.8%)–Ru^{3+} (0.8%)–V_2O_5 (17%); (5) $PdCl_2$–$RuCl_3$–V_2O_5 (17%); not activated at high temp to eliminate Cl^-. All supported on α-Al_2O_3.

and it was, therefore, assigned to V^{4+} centers existing within the V_2O_5 lattice. The g-value and the line width of the signal were measured to be:

$$g = 1.970 \pm 0.005,$$
$$\Delta H_{\text{peak-to-peak}} = 100 \sim 200 \text{ G} \quad \text{(see Fig. 2).}$$

Pentavalent vanadium oxide V_2O_5 is known to host many V^{4+} centers created by oxygen vacancies, and the g-value given above is consistent with the known g-value of other V^{4+} systems, e.g., V^{4+} in TiO_2, or VO^{2+} in various ligands. The broad line width is mostly due to unresolved hyperfine structure due to ^{51}V nuclei ($I = 7/2$, natural abundance ~100%) with large magnetic moments ($\mu = 5.14$ nuclear magneton). No other signal attributable to either PdO or V_2O_5 phase was observed within the temperature range 77°K to room temperature.

TABLE 3

DEPENDENCE OF V^{4+} CONCENTRATION ON CATALYST HISTORY

Catalyst	V^{4+} concn (10^{19} ions/g cat) Fresh cat	 Reduced[a]	 Oxidized[b]
V_2O_5–Al_2O_3	5	6	5
Pd–V_2O_5–Al_2O_3	6	12	9
Pd–Ti–V_2O_5–Al_2O_3	1	12	4

[a] Fresh catalyst exposed to C_2H_4/H_2O stream for 0.5 hr at 140°C.

[b] Reduced catalyst from a after exposure to O_2 for 0.5 hr at 140°C.

If the role of V_2O_5 in the Pd–V_2O_5 system is the reoxidation of Pd(O) to Pd(II), as proposed above, there should be a significant increase in the V^{4+} concentration when the catalyst is exposed to an C_2H_4–H_2O stream and a corresponding decrease when the catalyst so reduced is exposed to an O_2 stream at the reaction temperature. Shown in Table 3 are the V^{4+} concentrations, determined by ESR, of various catalysts as freshly prepared, after exposure to an C_2H_4–H_2O stream for 0.5 hr at 140°C, and after subsequent exposure to an O_2 stream for 0.5 hr at 140°C. The V^{4+} concentrations were determined by comparison with the spectrum of $(NH_4)_2SO_4$ containing 5 wt % of $VOSO_4$. A representative set of ESR spectra obtained is shown in Fig. 2. No significant additional change was noted when the exposure period was lengthened to 1 hr thus indicating that the system becomes effectively saturated within the period of 0.5 hr. The results show conspicuously that a system containing only V_2O_5 on α-Al_2O_3 is not significantly reduced by an C_2H_4–H_2O stream, nor oxidized by O_2 at 140°C. In contrast, the Pd–V_2O_5–α-Al_2O_3 system shows pronounced redox behavior under the same condition, and the behavior is even more pronounced in the case of Pd–Ti–V_2O_5–α-Al_2O_3. Most interestingly, it was found that the amplitudes of the redox cycles noted in these systems are in the same order of magnitude as the concentration of Pd atoms deposited. These results indicate strongly that palladium is the locus for both ethylene oxidation (catalyst reduction) and for reoxidation of the reduced system. The reduction–oxidation cycle described above was repeated several times on the same sample with full repro-

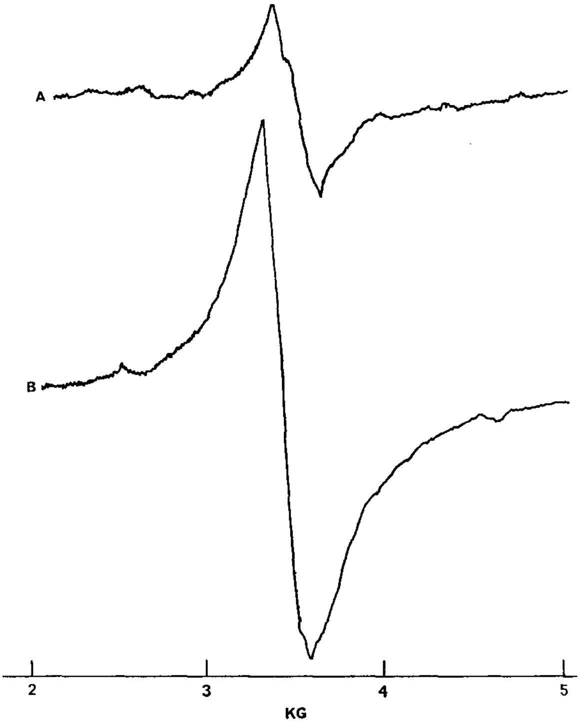


FIG. 2. ESR spectra of Pd-V_2O_5-alumina before (A) and after (B) exposure to C_2H_4/H_2O stream for 0.5 hr at 140°C.

ducibility further supporting the idea that the Pd-V_2O_5 system is capable of performing the redox cycle in a catalytic manner. The ESR examination of numerous catalyst samples through redox cycles also showed that the catalytic activity of the preparation was directly related to the size of the redox well.

The electronic configuration of Pd^{2+} is $4d^8$, and it is not surprising that the catalyst Pd-V_2O_5-alumina does not exhibit any ESR signal attributable to Pd^{2+} ions. Large anisotropy and extremely short relaxation time make the detection of the ESR signal of these ions difficult. The detection of the ESR signal of monovalant Pd^+ ion ($4d^9$), on the other hand, should not be as difficult. The failure to detect the signal attributable to Pd^+ implies extremely facile, if not spontaneous, transfer of electrons from Pd^0 to and V_2O_5 matrix, hence a strong and stable interaction between them.

The large changes observed in $[V^{4+}]$ imply substantial electron transfer in and out of the system. Titanium, when present, is believed to act on the V_2O_5 phase as a p-type dopant. As such, it should lower the Fermi level of the system, and create a depletion layer near the surface, thus increasing the mobility of the electrons and making the whole system more "reducible." The effect of the p-type doping was also seen in the line width of the V^{4+} signal of the reduced catalysts. The V^{4+} signal of Pd-Ti-V_2O_5 was found to be much narrower than that of Pd-V_2O_5 (see Fig. 3). Since the concentration of V^{4+} was nearly the same in these catalysts, the narrowing of the signal in Pd-Ti-V_2O_5 is attributed to the delocalization of the paramagnetic electron, reflecting the increased mobility.

Kinetic Results

The rate of reaction of ethylene over the Pd-X-V_2O_5 on α-Al_2O_3 catalysts showed only a very slight dependence on [Pd] at concentrations above the 0.1% wt level.

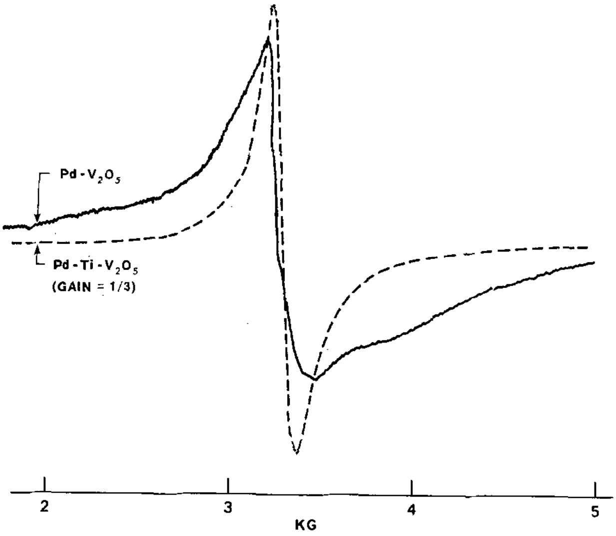


FIG. 3. ESR spectra of Pd-V_2O_5 alumina and Pd-Ti-V_2O_5-alumina after exposure to C_2H_4/H_2O stream for 0.5 hr at 140°C.

The data in Fig. 4 indicate that increasing the palladium concentration from 0.01 to 0.8%, caused only a twofold increase in activity. Very efficient utilization of palladium was evident in the catalysts at low palladium concentration. A catalyst containing 0.01% (by wt) Pd and operated with high space velocity at 180°C and 215 psia exhibited a turnover time (mol C_2H_4 conv/liter cat/sec)/(mol Pd/liter cat) of 2 sec, assuming all palladium ions to be equally active. The concentration of the vanadium oxide component did not significantly affect the rate, provided that the V/Pd ratio was $\gg 1$.

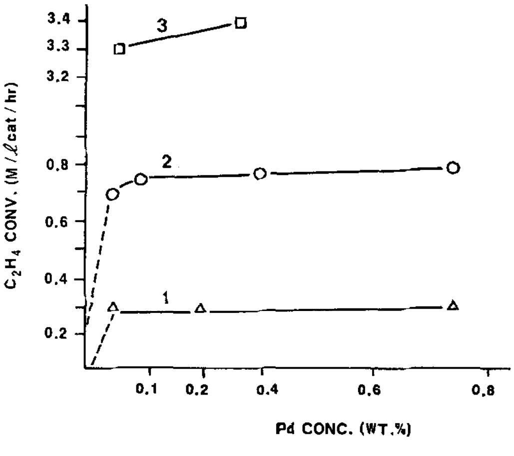


FIG. 4. Catalytic activity for C_2H_4 oxidation as a function of [Pd]: (1) Pd-V_2O_5 (17%) via palladium chloride; reaction cond. 140°C, 1 atm, tube reactor. (2) Pd-V_2O_5 (17%) via palladium polyvanadate; reaction cond. 146°C, 7 atm, recirc, back-mixed reactor. (3) Pd-Ti (0.4%)-V_2O_5 (17%) via palladium chloride: reaction cond. 170°C, 7 atm, recirc. back-mixed reactor.

The oxidation of ethylene was observed to be partial positive order in C_2H_4, O_2, and H_2O over a large range of concentrations. The dependence was complex, however, due to the existence of diffusional effects. At C_2H_4/O_2 ratios approaching 1, the reaction became essentially zero order in ethylene. In addition, at high H_2O concentrations (the exact level depending on the total pressure), the reaction became negative order in H_2O and there was irreversible damage to the catalyst.

Determination of the thermal dependence of these reactions affords values for the apparent activation energies for ethylene conversion and acetaldehyde formation in the range of 4–6 kcal/mole (Fig. 5). These low values are an indication of diffusional rather than kinetic control. The presence of diffusional limitations was confirmed by experiments in which the rate was shown to depend on the partial pressure of the nitrogen carrier gas. The apparent energies of activation for acetic acid and CO_2 for-

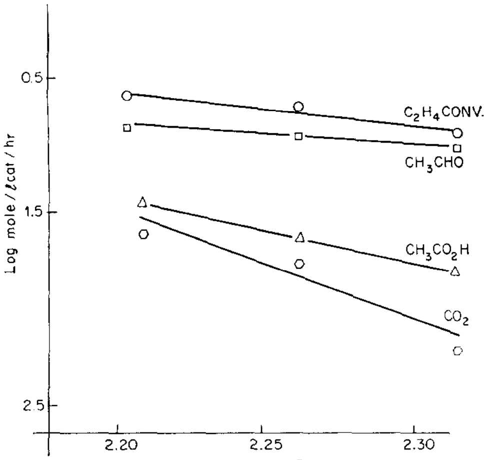
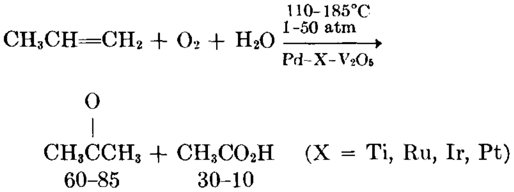


FIG. 5. The effect of temperature on product formation.

mation are in the range of 22–30 kcal/mole, depending on the precise composition of the catalyst.

Examination of the effect of the products on the rate of reaction revealed that acetaldehyde does not inhibit the conversion of ethylene but that acetic acid has a marked but reversible effect. Acetylene has no effect on these catalysts' activity. Compounds such as inorganic chlorides or H_2S, which are extremely good ligands for Pd, are irreversible inhibitors.

Although the emphasis of this research was on the oxidation of ethylene, extensive work was also done with propylene. Propylene is converted efficiently to acetone and acetic acid.



$$CH_3CH{=}CH_2 + O_2 + H_2O \xrightarrow[Pd\text{-}X\text{-}V_2O_5]{110\text{-}185°C,\ 1\text{-}50\ atm} \underset{60\text{-}85}{CH_3\overset{\overset{O}{\|}}{C}CH_3} + \underset{30\text{-}10}{CH_3CO_2H} \quad (X = Ti, Ru, Ir, Pt)$$

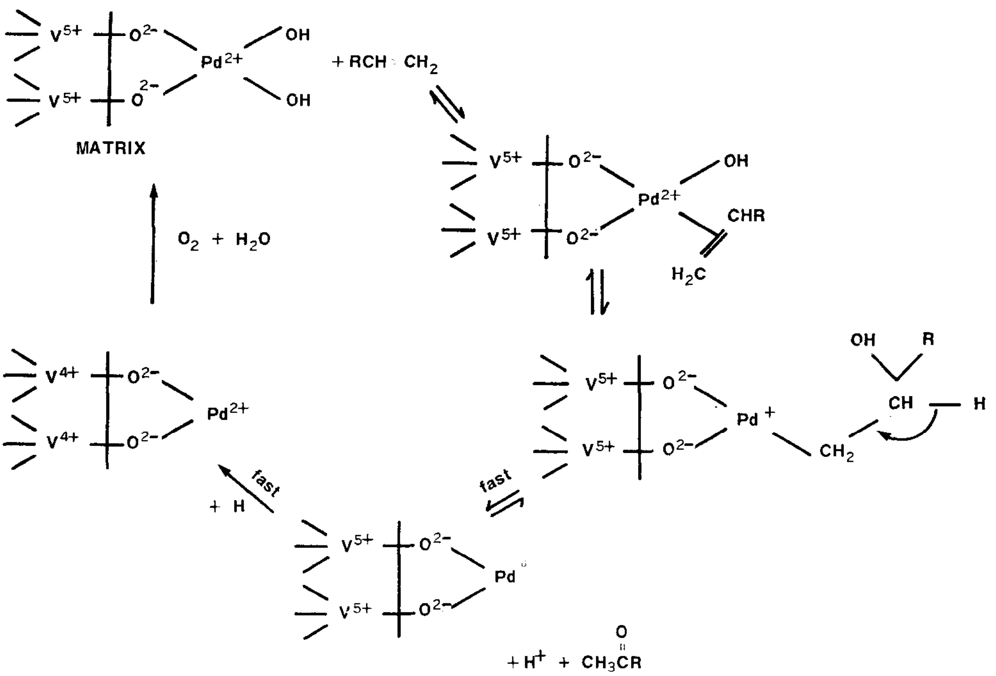
At most, traces of propionaldehyde or propionic acid were present in the effluent. Experiments were carried out under the conditions of both Tables 1 and 2 and propylene was oxidized 0.6× and 0.5× as fast as ethylene, respectively. The rate of oxidation of butenes was substantially slower than that of the propylene. Furthermore, in the reaction of butene, maleic acid and coke were formed and had a significant and harmful effect on catalyst performance.

DISCUSSION

The evidence accumulated on the nature of the organic reactions taking places on the Pd–X–V_2O_5 catalysts indicates a close relationship to the mechanism established for the solution phase, $PdCl_2$-catalyzed chemistry (*7*). In particular, the oxidation appears to involve coordination of both an olefin and a hydroxyl to Pd(II) followed by direct formation of the carbonyl compound and the reduction of the V_2O_5 substrate via the palladium center and finally reoxidation of the vanadium oxide by oxygen.

The ESR experiments provided important information both on the role of palladium and on the vanadium pentoxide phase. By monitoring the V^{4+} signal it is evident that a system containing Pd and V_2O_5 shows redox behavior under conditions where V_2O_5 alone does not. These results indicate strongly that palladium is the site of both ethylene oxidation (catalyst reduction) and, reoxidation of the reduced system. The large changes observed in $[V^{4+}]$, moreover, imply substantial electron mobility within the system. The ability of palladium to facilitate the reduction of vanadium pentoxide has also been observed by French workers (*9*), who apparently used chemical rather than spectroscopic techniques to follow the changes in V^{4+}. Those authors did not comment on effects of Pd on the rates of oxidation.

The exact environment of the palladium species in the Pd–X–V_2O_5 catalysts was not determinable by direct spectroscopic, structural or chemical studies. The fact that supported salt systems (e.g., $PdCl_2$ + $CuCl_2$), which are known to contain Pd(II) ions, behave like the Pd–X–V_2O_5 systems, at least for a short while before becoming deactivated, strongly suggests that Pd^{2+} species are the active centers in our catalyst as well. Further confirmation comes from a comparison of the selectivity and rates of olefin oxidations over Pd–X–V_2O_5 catalysts and in the solution Wacker process. In par-



ticular, both catalysts are more active for ethylene than for propylene oxidation (1.7–2 times here and 3 times with the Wacker) (*10*), and both oxidize propylene specifically to acetone. The relative rates of ethylene and propylene oxidation essentially precludes a mechanism for carbonyl formation involving hydration followed by oxidation. Electrophilic attack on a double bond is typically 1–2 orders of magnitude faster for propylene, which affords a secondary carbonium ion, than for ethylene (*11*). Also, in such a mechanism the critical role of palladium would be difficult to explain since coordination of olefins to Pd(II) involves a significant component of back donation which activates the olefins for nucleophilic rather than for electrophilic substitution. A final point of similarity between our heterogeneous system and the aqueous Wacker system, is the unique activity of Pd. Under both sets of conditions, and particularly in our case, other noble metals show only insignificant activity.

It was not possible to establish the source of the hydrogen that shifts during the oxidations of ethylene and of propylene. In the solution phase chemistry (*12*) and in the vapor-phase oxidation of ethylene by Pd–Au sponge (*13*), the shift is internal. It is accordingly attractive to hypothesize a similar sequence in our reactions, but attempts to verify this by deuterium labeling were negated by acid-catalyzed scrambling.

The mechanism that emerges from the above considerations is shown below. All evidence indicates that the Pd–X–V_2O_5 catalyst contains a unique link between the single Pd(II) ions and the semiconducting V_2O_5 phase.

CONCLUSIONS

Vapor-phase oxidation of ethylene to acetaldehyde and propylene to acetone over catalysts typically containing palladium, titanium, and vanadium pentoxide, is an example of a new generation of heterogeneous catalysts which operate on the double bond of olefins (*14*). These catalysts have selectivities and activities similar to those of their homogeneous analogs and substantial similarities to solution phase mechanisms are evident. The Pd–X–V_2O_5 system for olefin oxidation may provide a synthetic alternative to homogeneous syntheses.

EXPERIMENTAL METHODS

Reaction Conditions

Reactions were carried out in both glass and steel tubular reactors with 1 in. i.d. and also in a recirculating, back-mixed reactor which has been previously described (*8*). High purity gases were utilized. The concentrations of CO_2, C_2H_4, C_3H_6, CH_3CHO and CH_3COCH_3 in the gaseous effluent were determined by gc using a Poropak Q column; Linde 5-A molecular sieves were utilized for O_2 and N_2 and CO analyses. Condensates were analyzed by titration and, subsequently, by either NMR spectroscopy or gc.

Catalyst Preparation

Preparation of a Pd–X–V_2O_5 catalyst typically involved several steps. First, a V_2O_5 phase was prepared on the α-Al_2O_3 (1–2.8 m^2/g) support, for example, by spray-drying a solution of ammonium vanadate and then activating in air at 350–500°C. In cases where $X = Ti$, the titanium was usually introduced along with the vanadium salt to ensure its doping into the V_2O_5 matrix. The palladium was then applied to the supported V_2O_5 phase in the form of a suitable salt such as the chloride, acetate, or vanadate. A final calcination step afforded the finished catalyst system. X-Ray analyses of this material showed the presence of V_2O_5 crystallites with dimensions of $\sim$500 Å, in addition to the α-Al_2O_3 phase. No phases attributable to palladium metal or oxide were visible.

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REFERENCES

1. SMIDT, J. R., HAFNER, W., JIRA, R., SEDLMEIER, J., SIEBER, R., RUTTINGER, R., AND KOJER, H., *Angew. Chem.* **71,** 176 (1959).
2. "Ethylene and Its Industrial Derivatives" (S. A. Miller, Ed.), p. 658. Ernest Benn, London, 1969.
3. (a) Ethylene-Vinyl acetate: French Pat. 1,397,083, 1,407,526 (1965); (b) Methanol-Acetic Acid: R. G. Schultz and P. D. Montgomery, *J. Catal.* **13,** 105 (1969).
4. *It. Pat.* 631868, 640,456 (1962); *U. S. Pat.* 3,379,651 (1968); Ger. Pat. 1,049,845 (1959); *U. S. Pat.* 3,057,915 (1962); *U. S. Pat* 3,419,-618 (1968); *U. S. Pat.* 3,439,044 (1969).
5. *U. S. Pat.* 3,240,805 (1966); *Fr. Pat.* 1,536,185 (1968); 1,568,742 (1969).
6. *Neth. Pat.* 6,716,263 (1968).
7. SMIDT, J., HAFNER, W., SEDLMEIER, J., JIRA, R., AND RUTTINGER, R., *Chem. Ind. Genie Chem.* **101,** 291 (1969).
8. BERTY, J. M., HAMBRICK, J. O., AND ULLOCK, D. S., Prepr. 42e, presented: AIChE Symp. High Pressure Technol., Part II, New Orleans (Mar. 16–20, 1969).
9. BELJEAN, C., BOUNTRY, P., AND MONTARNAL, R., *C. R. Acad. Sci. C* **270,** 257 (1970).
10. HENRY, P. M., *J. Amer. Chem. Soc.* **88,** 1595 (1966).
11. HENRY, P. M., *in* "Advances in Chemistry Series," Vol. 70, Amer. Chem. Soc., Washington, DC, 1968.
12. SMIDT, J., HAFNER, W., JIRA, R., SIEBER, R., SEDLMEIER, J., AND SABEL, A., *Angew. Chem.* **74,** 93 (1962).
13. GERBERICH, H. R., CANT, N. W., AND HALL, H. K., *J. Catal.* **16,** 204 (1970).
14. Ref. 3a and for ethylene to acrylonitrile: *Fr. Pat.* 1,441,897 (1966).