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Heterogeneous Catalyst for Alcohol Oxycarbonylation to Dialkyl Oxalates

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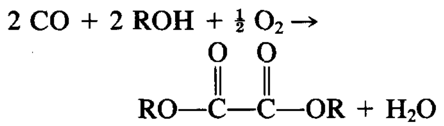
A titanium-promoted palladium–vanadium pentoxide catalyst for oxycarbonylation of alcohols (ROH) to dialkyl oxalates has been developed. Dialkyl oxalates may be hydrogenated to ethylene glycol and ROH and the latter can be recycled. Optimum oxalate selectivity is 90%, with CO_2, methylal, and methyl formate as major by-products. The oxycarbonylation reaction involves a surface Pd(II)/Pd^0 couple. The V(V)/V(IV) couple serves as a co-oxidant for Pd. Molecular oxygen reoxidizes V(IV) to V(V). The titanium promoter improves overall catalyst activity by a factor of 5. Oxycarbonylation kinetics are first order in ROH and CO. Relative rates of oxalate ester formation with methanol, ethanol, 1-propanol, and 1-butanol are consistent with nucleophilic attack of alcohol on a surface oxalate species. The effect of Pd loading on activity suggests Pd is associated with two surface V sites.

INTRODUCTION

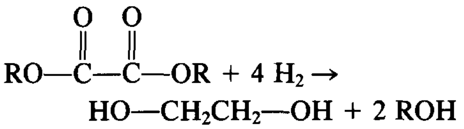
In recent years there has been a great deal of interest in the production of ethylene glycol via synthesis-gas-based routes. Current commercial technology involving direct ethylene oxidation to ethylene oxide and subsequent hydrolysis relies on a stable and economical supply of ethylene. There has been considerable price escalation in the basic petrochemical feedstocks since the 1974 oil embargo. Synthesis gas could be the more flexible feedstock of the future since it can be produced from a variety of carbon sources.

Historically, the first major process for commercial ethylene glycol production (*1*) from synthesis gas was the acid-catalyzed carbonylation of formaldehyde to glycolic acid. The acid was then hydrogenated to the desired product. Due to major corrosion problems and the relative inexpensiveness of ethylene, this process was abandoned in favor of the ethylene oxide route. There has been recent research activity in this formaldehyde carbonylation process (*2*), but again strongly acidic conditions are employed. The similar route of formaldehyde hydroformylation to glycoaldehyde followed by hydrogenation is also attracting attention (*3*). Considerable progress has been made in the direct formation of ethylene glycol from synthesis gas (*4*).

The reaction discussed in this paper is another variant of the synthesis-gas-based routes of ethylene glycol. Dialkyl oxalate esters can be formed from the oxidative carbonylation of carbon monoxide and an alcohol (*5*):



$$2\,CO + 2\,ROH + \tfrac{1}{2}\,O_2 \rightarrow RO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + H_2O \quad (1)$$



$$RO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + 4\,H_2 \rightarrow HO{-}CH_2CH_2{-}OH + 2\,ROH \quad (2)$$

The dialkyl oxalate ester can then be hydrogenated to yield ethylene glycol (Eq. (2)). This route offers the advantages of milder reaction conditions and higher selectivities to the desired product. The reaction is generally catalyzed by platinum group metals, notably palladium, in conjunction with a co-oxidant. The first reported catalysis of

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TABLE 1

Performance of Palladium on Metal Oxide Catalysts[a]

No.	Metal oxide	Oxalate	CO_2	Others[b]	Oxalate productivity (g/g cat./hr)
1	Mn_2O_3	93	7	0	0.77
2	V_2O_5	74	26	0	0.38
3	Mn_3O_4	87	13	0	0.38
4	Co_3O_4	79	21	0	0.36
5	Fe_2O_3	84	16	0	0.30
6	Fe_3O_4	79	21	0	0.28
7	SnO_2	67	33	0	0.23
8	CeO_2	73	27	0	0.21
9	SnO	38	50	12	0.17
10	CuO	70	30	0	0.13
11	Nd_2O_3	60	40	0	0.11
12	ZrO_2	67	33	0	0.11
13	TiO_2 (rutile)	56	44	0	0.09
14	TiO_2 (anatase)	43	57	0	0.06
15	WO_3	24	76	0	0.04
16	Bi_2O_3	0	11	89	0
17	Nb_2O_5	0	100	0	0
18	Sb_2O_5	0	100	0	0

Note. Methanol oxycarbonylation at 100°C for 15 min at 144 atm CO and 28 atm air using 1.25 wt% slurry of catalyst in methanol. Total oxalate includes DMO and oxalic acid.

[a] Palladium (3%) on metal oxides.

[b] Dimethoxymethane.

this reaction by (*6, 7*) was performed in a homogeneous solution phase using palladium salts and copper, or iron, as the co-oxidants.

Other co-oxidants, such as quinones, have been reported (*8*) along with a myriad of oxidative coupling agents (*9*). Progress in this area has been made using palladium salts supported on carbon (*5*). However, reactive co-oxidants such as alkyl nitrite are required for high oxalate productivities (*5*).

We studied numerous one- and two-electron redox metal oxides and found several to function quite effectively as co-oxidants for palladium in heterogeneous palladium-metal oxide catalysts for alcohol oxycarbonylation. Phosphorous and titanium-promoted palladium–vanadium oxide catalysts are especially effective. These catalysts were investigated because of the similarities in active catalysts for the oxidative carbonylative process and catalyst systems for the Wacker reaction, involving the oxidation of ethylene to acetaldehyde. Evnin *et al.* have described (*10*) the use of palladium supported on vanadium as a heterogeneous vapor-phase catalyst for acetaldehyde formation. This paper discusses how similar systems, and others, affect the oxidative carbonylation of alcohols to alkyl oxalates.

EXPERIMENTAL

Redox Oxide-Supported Palladium Catalysts

The metal oxides listed in Table 1 were purchased from Alfa Products and palladium dichloride (Alfa Products) was loaded via the incipient wetness method using 1 *N* ammonium hydroxide solution. The incipient wetness method involves impregnating the dry solid with a volume of solution just sufficient to fill the pore volume of the dried solid. This was followed by drying under vacuum at 90 and 400°C calcination for 16 hr.

Preparation of Vanadium–Titanium Oxide Support

A procedure similar to that reported by Brockhaus (*11*) was followed for the preparation of the vanadium–titanium oxide support. A homogeneous mixture of vanadium and titanium oxides was prepared by addition of titanium tetrachloride (Alfa Products) to an aqueous hydrochloric acid slurry of vanadium pentoxide (Alfa Products). The addition was carried out at a rate such that the maximum temperature was 40°C. The titanium–vanadium oxide mixture was precipitated from solution by addition of ammonium hydroxide solution. During the precipitation, the pH was maintained at 1.4–2.1 and the temperature was 40°C. The pH was adjusted to 5.7 and the resulting precipitate was filtered, thoroughly washed, dried under vacuum at 80°C, and calcined at 400°C for 16 hr. The atomic proportion of titanium : vanadium was 1 : 1.

The gentle treatment given below improved selectivity and activity of a titanium vanadate-based catalyst employed in acetic acid production (*11*). During the process, the catalyst was slightly etched by treatment with aqueous hydrochloric acid so that a small amount of support was dissolved and removed. Thus, there was a slight change in the atomic proportion of titanium to vanadium. An analogous etching procedure was followed to obtain a more selective and active catalyst. The calcined vanadium–titanium oxide was treated with 15% hydrochloric acid at 50°C for 5 min. This was followed by careful washing with water until the pH value rose to 4, drying under vacuum at 150°C, and by calcining at 400°C for 16 hr.

Palladium on Vanadium–Titanium Oxide Catalyst

By incipient wetness, palladium dichloride (Alfa Products) dissolved in 1 *N* ammonium hydroxide was loaded on the titanium vanadate support. This was followed by drying under vacuum at 90°C and calcining at 400°C for 16 hr.

Preparation of Vanadium Phosphate Support

The vanadium phosphate support was prepared by a previously disclosed method involving the reaction of orthophosphoric acid with a vanadium oxycompound (*12*). Vanadium pentoxide was suspended in a 2 : 3 mixture of benzyl alcohol and 2-butanol (Aldrich Chemical Co.). The mixture was refluxed for 4 hr during which time partial reduction of V(V) to V(IV) occurred. The resulting slurry was reacted with orthophosphoric acid (Alfa Products) and refluxed for 10 hr with continuous removal of the 2-butanol/water azeotrope. The solids were collected, washed with 2-butanol, dried under vacuum, and calcined at 400°C for 16 hr. The atomic proportion of phosphorus : vanadium ranged from 0.5 : 1 to 2 : 1. Palladium was loaded onto the vanadium phosphate support by the same method described for vanadium–titanium oxide.

Reactor Apparatus

The oxidative carbonylation reactions were carried out in a 500-cm^3 Hasteloy-C autoclave equipped with a Magnadrive stirrer and appropriate temperature and pressure controls. A typical run called for charging the reactor with a 1.25 wt% slurry of catalyst in methanol, 144 atm CO and 28 atm air. The reactions were usually carried out for 15 min at 100°C after which time the resulting gas and liquid filtrate were analyzed for product composition. The solids collected by filtration were in some cases recycled or analyzed for V^{4+}/V^{5+} split, surface area, and % Pd, V, promoter composition.

GC Method

Reaction product filtrates were analyzed on a Varian 3700 gas chromatograph equipped with a Shimadzu C-RIA chromatopac integrator. The FID analysis was carried out on a 6-ft × 0.25-in. glass column packed with 10% SP 1000 on 80/100 Supelcoport (Supelco). A column temperature program ranging from 70 to 230°C was employed and diglyme (Aldrich) was the internal standard.

Oxalate Method

A total oxalate analysis, to account for both dimethyl oxalate and oxalic acid in product filtrates, was carried out by initial hydrolysis of the ester in 0.01 *N* HCl. Upon complete hydrolysis, the solution was titrated with 0.01 *N* NaOH to determine milliequivalents of oxalic acid.

V^{4+}/V^{5+} Titrations

The V^{4+}/V^{5+} split was determined by initially dissolving the vanadium from the recovered catalyst. This was carried out by adding a 50% sulfuric acid solution to the solids and boiling for 1 hr. The filtrate containing the vanadium(IV) and (V) salts was titrated with 0.1 *N* permanganate solution to determine the meq of V(IV). The resulting oxidized filtrate was then reduced with sodium sulfite. A second titration with permanganate solution gave the total meq of vanadium. The meq of V(V) was determined by taking the difference, i.e., meq total − meq V(IV).

RESULTS

Pure Redox Oxide Supports

The results for the 18 metal oxides studied in decreasing order of catalytic activity are summarized in Table 1. The reactions were carried out under identical conditions: 1.25 wt% catalyst slurry in methanol; 100°C; 2100 psig CO; 400 psig air. Product selectivities and oxalate productivities are also shown in the table. Pd/Mn_2O_3 was the most active catalyst for oxalate formation. Bi_2O_3-, Nb_2O_5-, and Sb_2O_5-supported Pd catalysts did not give any oxalates. But, the Pd/Bi_2O_3 did produce dimethoxymethane with 89% selectivity. The fact that a great variation in activity exists clearly rules out the possibility that leached-out palladium species or other metal oxide species were responsible the reactions observed despite that various low levels of palladium and the metals have been found in the products. (vide infra).

TABLE 2

P and Ti Promoters for 3% $Pd-V_2O_5$

Promoter (M)	None	P	P	Ti
V/M mole ratio	—	1:2	1:0.5	1:1
V^4/V^5 split	0/100	22/78	5/95	10/90
% Selectivity				
Total oxalate	74	94	92	91
CO_2	26	3	4	9
Rate (mmole oxalate/g cat. min)	0.054	0.31	0.47	0.66
Surface area, m^2/g	4.4	4.9	4.4	35

Note. Methanol oxycarbonylation at 100°C for 15 min at 144 atm CO and 28 atm air using 1.25 wt% slurry of catalyst in methanol. Total oxalate includes DMO and oxalic acid.

Phosphorus and Titanium Promoters

Phosphorus is known to affect the content and the catalytic activity of vanadium oxide catalysts for butene oxidation to maleic anhydride (*11, 12*). Similar effects are well known for titanium promoters (*10, 15–17*). The results in Table 2 show a significant improvement in the rate of dimethyl oxalate formation and selectivity with addition of phosphorus or titanium promoters to the 3% $Pd-V_2O_5$ catalyst. The balance of the products were methylal, dimethyl carbonate, and methyl formate. Low levels of V(IV) give the largest improvement in activity. Similar results have been reported on the effect of V(IV) content on 2-propanol decomposition over vanadium oxide catalysts (*18*). The $V_2O_5-TiO_2$ catalyst preparation yields catalysts with significantly higher surface areas. In view of the superior activity of the titanium-promoted catalyst, it was selected for further study.

Catalyst leaching has been observed with some of the catalyst screened. Both 1–10 ppm levels of palladium and 100–1000 ppm

TABLE 3

Effect of Reaction Time

Time (min)	15	60
% Selectivity		
DMO	75	38
Oxalic acid	16	27
CO_2	9	16
DMC	tr	tr
MF + MA	tr	19
$\frac{\text{mmole oxalate}}{\text{g cat. min}}$	0.66	0.49

Note. Conditions: 100°C, 144 atm CO and 28 atm air, 1.25 wt% slurry of 3% Pd–V_2O_5–TiO_2 catalyst in methanol. DMO, dimethyl oxalate; DMC, dimethyl carbonate, MF, methyl formate; MA, methylal.

TABLE 4

Effect of V(IV) Level

Recycle No.	1	2	3	4
% Selectivity				
Oxalate	61	60	73	82
CO_2	18	34	21	18
DMC	2	0	0	0
MF + MA	18	6	6	0
V^5/V^4	85/15	35/65	16/84	15/85
$\frac{\text{mmole oxalate}}{\text{g cat. hr}}$	0.49	0.11	0.062	0.066

Note. Conditions: 1.25 wt% slurry of catalyst in methanol at 100°C for 1 hr at 144 atm CO and 28 atm air. DMC, dimethyl carbonate; MF, methyl formate; MA, methylal. Oxalate includes DMO and oxalic acid.

levels of vanadium have been found in solution in the reaction products. The question of whether the dissolved species are contributing significantly to the observed reaction must be addressed before any attempts are made to interpret the experimental results. Careful experiments were carried out separately with the product solution containing dissolved materials and the recovered solid catalysts. In all cases, the solutions showed very little activity under identical reaction conditions while the solid catalysts retained their original activities. These experiments clearly established the heterogeneous nature of the catalysts. Moreover, spiking the reaction medium with oxalates showed no inhibition of catalyst activity. Fresh and recycled catalysts of palladium on vanadium–titanium oxide were used in autoclave runs conducted in the absence of CO. The methanol slurry spiked with 1 wt% oxalic acid and 0.5 wt% water was charged with nitrogen (144 atm) and air (28 atm) and stirred for 1 hr at 100°C. The total oxalate content remained unchanged and traces of carbon dioxide were detected confirming oxalate stability and negligible direct methanol oxidation under reaction conditions.

Longer run time, 60 vs 15 min, resulted in increased hydrolysis of dimethyl oxalate (DMO) to oxalic acid, Table 3. These results also imply that DMO, not oxalic acid is the initial reaction product.

The effect of V(IV) content on the V_2O_5–TiO_2 catalyst was studied in a series of 1-hr recycle experiments. Over a 1-hr run period, approximately 50% of the oxygen charged to the reactor system is consumed. The V(V) level of the recovered catalyst is thus more depleted than in a 15-min run. The results of 4 recycle experiments are shown in Table 4. These and other runs are shown in Fig. 1. Longer run times and higher oxygen conversion give lower overall selectivities to total oxalate (DMO plus oxalic acid). There is a clear optimum in activity when 10–20% of the total vanadium is present as V(IV). The vanadium oxida-

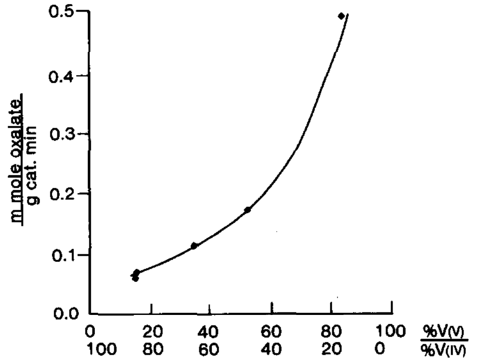


FIG. 1. Effect of V(IV) content on rate of DMO formation. Reaction conditions as in Table 3.

TABLE 5

Effect of Palladium Loading[a]

wt% Pd	0	1	2	3
% Selectivity				
Oxalate	57	58	62	65
CO_2	15	21	15	16
DMC	tr	tr	tr	tr
MF + MA	27	21	23	19
$\frac{\text{mmole oxalate}}{\text{g cat. min}}$	0.018	0.24	0.45	0.49

[a] All runs for 60 min at 100°C, same conditions as employed for Table 3.

tion state analysis were performed on recovered catalyst prior to changing to the next recycle.

Pd Loading

The Pd loading on the $Pd-V_2O_5-TiO_2$ catalyst was varied from 0 to 3 wt%. Results of 1-hr runs are shown in Table 5 and Fig. 2. Pd is an essential part of the catalyst system and activity is maximum at 2 to 3 wt% loading. A similar palladium loading effect was observed on a palladium-tin oxide catalyst for CO oxidation (*19*). Since the surface area (BET) of the V_2O_5/TiO_2 support is 35 m^2/g, about 2.0 wt% of palladium is needed to saturate the surface if two metal oxide centers are needed for each palladium (*10*). This is in good agreement with the results. It is also interesting to note that oxalate selectivity was not significantly affected by varying palladium loadings.

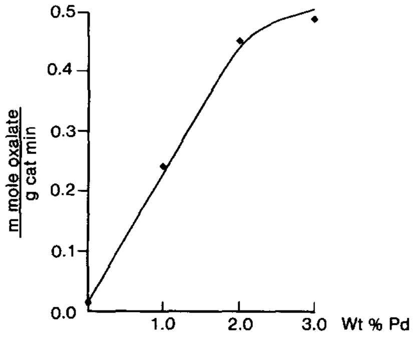


FIG. 2. Effect of palladium loading on activity of $V_2O_5-TiO_2$ catalyst. Reaction conditions as in Table 3.

Kinetics

Reaction kinetics as a function of various pressures of carbon monoxide and air were studied. The results are presented in Table 6. The reactor system volume is such that in all the kinetic runs, the partial pressure of oxygen changes by no more than 13% and carbon monoxide by no more than 2%. Thus the initial partial pressures listed in Table 6 are essentially constant over the reaction period. For either product, an empirical rate law may be written as

$$r = kP_{CO}^{x}P_{O_2}^{y} \quad (1)$$

$$\ln r = x \ln P_{CO} + y \ln P_{O_2} + \ln k. \quad (2)$$

Linear regression of the experimental rate data according to Eq. (2) thus yields values of x, y, and k for both total oxalate and carbon monoxide. The following equations account for 99% of the variance in oxalate rate and 97% of that in CO_2 rate

$$r(\text{oxalate}) = (6.52 \times 10^{-3})P_{CO}^{0.89}P_{O_2}^{0.14}$$

$$r(CO_2) = (6.89 \times 10^{-5})P_{CO}^{1.26}P_{O_2}^{0.35}.$$

Both oxalate and CO_2 formation are approximately first order in CO.

TABLE 6

Effect of CO and O_2 Pressure[a]

P_{CO} (atm)	P_{O_2} (atm)	Rate of formation[b]	
		Oxalate	CO_2
58.1	2.38	0.28	0.015
86.7	3.47	0.42	0.046
115.3	4.55	0.50	0.045
143.9	5.64	0.66	0.067
143.9	5.64	0.68	0.070
157.5	2.92	0.68	0.059
172.4	6.73	0.91	0.085

[a] Runs (15 min) at 100°C using 1.25 wt% slurry of 3% $Pd-V_2O_5-TiO_2$ catalyst in methanol.

[b] In mmole product/g cat./min.

TABLE 7

Effect of Alcohol Structure[a]

Alcohol	mmole oxalate / g cat. hr	Relative rates Oxalate formation	Tosylate solvolyses[b]
Methanol	0.66	1.00	1.00
Ethanol	0.35	0.53	0.58
1-Propanol	0.17	0.27	0.47
1-Butanol	0.045	0.07	0.36

[a] At 100°C, 144 atm CO, 28 atm air, 15 min.
[b] From Refs. (*18, 19*).

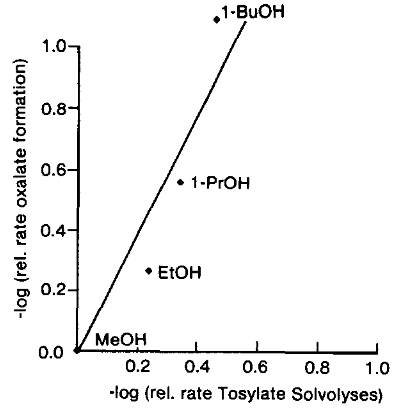
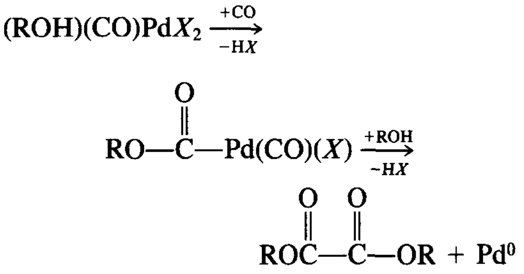


FIG. 3. Linear free-energy relationship between relative rates of tosylate solvolysis and oxycarbonylation.

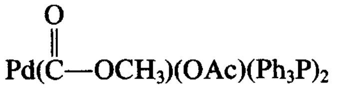
The effect of different alcohols on the rate of oxalate production is shown in Table 7. Methanol is most reactive and the relative reactivities of the different alcohols parallel those found in methyl tosylate solvolysis (*20, 21*). This suggests that nucleophilic attack of free or adsorbed alcohol is involved in (or prior to) the rate-limiting step for oxalate formation. A good linear free-energy relationship is shown in Fig. 3.

Fenton (*6*) studied the homogeneous palladium-catalyzed formation of dialkyl oxalates from CO and alcohol and postulated the sequence



$$(\mathrm{ROH})(\mathrm{CO})\mathrm{Pd}X_2 \xrightarrow[-\mathrm{H}X]{+\mathrm{CO}} \mathrm{RO{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}Pd(CO)}(X) \xrightarrow[-\mathrm{H}X]{+\mathrm{ROH}} \mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{OR} + \mathrm{Pd}^0$$

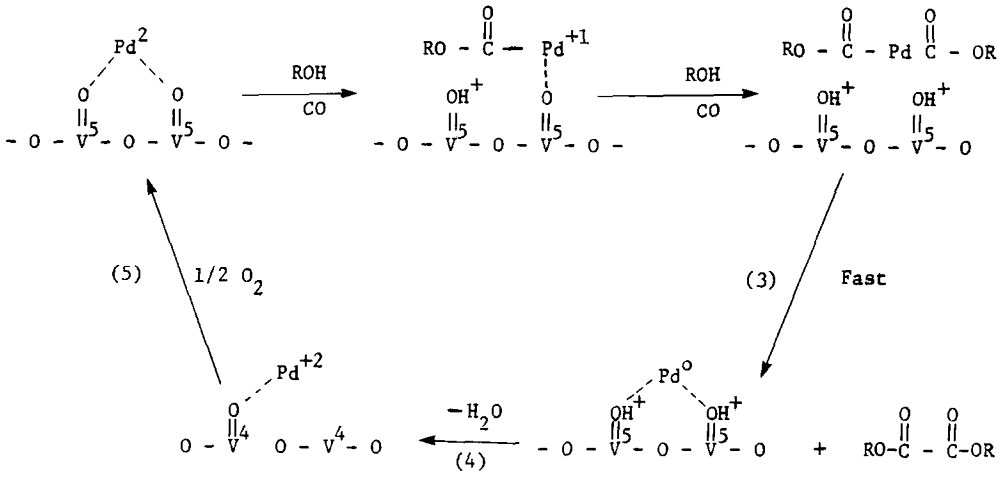
Rivetti and Romano (*22, 23*) studied the reaction using palladium(II) acetate in methanol solvent in the presence of triphenylphosphine at moderate (300–750 psi) carbon monoxide pressure. Above 50°C, dimethyl oxalate, acetic acid, and palladium(0) were produced. Below 50°C, the following monocarboalkoxy complex was isolated:



$$\mathrm{Pd}(\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{OCH_3})(\mathrm{OAc})(\mathrm{Ph_3P})_2$$

The analogous dicarboalkoxy complex could not be isolated from low-temperature reactions but was independently synthesized. $\mathrm{Pd(COOCH_3)_2(Ph_3P)_2}$ was found to be stable as a solid but decomposed in methanol solution to give dimethyl oxalate and palladium(0) carbonyl–triphenylphosphine complexes. They thus postulated a reaction mechanism similar to Fenton's. Considering the relative stabilities, the rate-limiting step is implied to be conversion of the monocarboalkoxy complex to the dicarboalkoxy complex which rapidly decomposes to (reductively eliminates) dimethyl oxalate and palladium(0). Thus dimethyl oxalate formation would be expected to be first order in carbon monoxide. Rivetti and Romano did not study reaction kinetics in their system but the increase in dimethyl oxalate yield with increasing CO pressure is quantitatively consistent with first-order kinetics in carbon monoxide. A similar mechanism for the homogeneous reaction has been postulated by Henry (*24*).

The observed first-order dependence of oxalate formation on carbon monoxide pressure with the $\mathrm{Pd{-}V_2O_5{-}TiO_2}$ catalyst suggests a mechanism involving similar mono- and dicarboalkoxy palladium surface species



An unambiguous assignment of oxidation states is not possible. The above assignments are for "electron counting" purposes.

The rate-limiting step of the reaction is either formation of the dicarboalkoxy species or its decomposition to palladium(0) and oxalate. Both are consistent with first-order kinetics in carbon monoxide. The large effect of alcohol structure on oxycarbonylation rate suggests that formation of the dicarboalkoxy species is rate limiting. The good linear free-energy relation between relative rates of alcohol oxycarbonylation and reported relative rates of tosylate solvolysis suggest nucleophilic attack of alcohol on coordinated CO is involved in the rate-limiting step, reactions 1 or 2 in the scheme.

Redox interaction between palladium and vanadium pentoxide is well documented in the literature (*10, 25, 26*) as is the promoting effect of titanium. Evnin *et al.* (*10*) have shown that vanadium(V) reoxidizes palladium(0) to palladium (*11*) with formation of vanadium(IV). The latter is reoxidized to vanadium(V) by molecular oxygen. They showed that titanium(IV) promoted this electron transfer process. They postulated that palladium is associated with two surface vanadium sites.

This work has shown that similar palladium–vanadium–titanium oxide catalysts are quite effective for catalytic alcohol oxycarbonylation. Kinetics are consistent with a monocarboalkoxy palladium surface specie as the key reaction intermediate. The effect of palladium loading on activity implies palladium is associated with two vanadium sites.

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