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Heterogeneous Catalyzed Benzylic Acetoxylation of Methylated Aromatic Hydrocarbons

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The palladium-catalyzed acetoxylation of toluene to benzyl acetate is highly dependent on particle size. The rate of reaction is highest with 30–35 Å particles corresponding to a 0.33 dispersion. Catalysts prepared and reduced by controlled methods before being contacted with the reaction medium, *ex situ* catalysts, were found to yield lower reaction rates than catalysts prepared in the reaction medium, *in situ*. Potassium ion encapsulation in palladium during *in situ* preparation is a possible explanation for this result. Tin is required to reduce Pd^{2+} to Pd^0 in the *in situ* system, but is not required for the *ex situ* catalyst. The improvement in activity of the *ex situ* catalyst in the presence of tin may be due to the reducibility of Sn^{4+} to Sn^{2+} during oxygen-poor regimes. Results obtained with diverse methylated aromatic hydrocarbons indicate that the aromatic ring interacts with the palladium surface via π-donation before oxidation occurs.

INTRODUCTION

Benzylic aldehydes and alcohols are widely used as end products and intermediates in the flavors and fragrances industry. Benzaldehydes of particular interest are, for example, benzaldehyde (bitter almond flavor), 4-methoxybenzaldehyde (lilac fragrance), vanillin (vanilla flavor), 4-isopropylbenzaldehyde (intermediate in the synthesis of cyclamen aldehyde, a floral lily scent), 4-tertbutylbenzaldehyde (intermediate in the synthesis of lilial, lily of the valley fragrance), piperonal (flower blossom fragrance), and 3,4-dimethoxybenzaldehyde (forest scent) (*1*).

Benzylic alcohol is used as a base chemical for the dilution of perfumes, as a local anesthetic and for applications in the textile industry. Benzylic alcohols may also serve as intermediates for the synthesis of insecticides, such as the synthesis of permethrin by esterification of 3-phenoxybenzyl alcohol by a chrysanthemic acid derivative (*1*).

The direct, selective oxidation at the methyl group of methylated aromatic hydrocarbons (MAHs) could be a particular attractive synthetic route to access of these end products and intermediates. Unfortunately, oxidation reactions generally do not stop at an intermediate stage, but rather continue on to the more thermodynamically stable products, such as benzoic acids, (*2*, *3*). This is particularly true at high substrate conversions.

One approach which has been employed to limit over-oxidation at high substrate conversions is the acyloxylation of MAHs, i.e., benzylic oxidation at the methyl group in the presence of a carboxylic acid, oxygen, and a catalyst to produce the corresponding benzyl carboxylates and dicarboxylates (*4–7*), Eqs. (1) and (2). The resulting benzyl carboxylates and benzyl dicarboxylates can then be easily hydrolyzed to yield benzyl alcohols and benzyl aldehydes, respectively, with regeneration of the carboxylic acid, Eqs. (3) and (4). Benzyl alcohol is usually not detected under normal acetoxylation conditions:

$$ArCH_3 + RCOOH + \tfrac{1}{2}O_2 \rightarrow ArCH_2O(O)CR + H_2O \quad (1)$$

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$$ArCH_2O(O)CR + RCOOH + \tfrac{1}{2}O_2 \rightarrow ArCH(O(O)CR)_2 + H_2O \quad (2)$$

$$ArCH_2O(O)CR + H_2O \rightarrow ArCH_2OH + RCOOH \quad (3)$$

$$ArCH(O(O)CR)_2 + H_2O \rightarrow ArCHO + 2RCOOH. \quad (4)$$

Acetic acid generally serves as the carboxylic acid, thus the term acetoxylation is employed. The palladium-catalyzed acetoxylation of toluene to benzyl acetate was first achieved with 40–45% selectivity at unknown toluene conversion (*8, 9*). This reaction was thought to be stoichiometric with respect to palladium acetate (i.e., turnover numbers less than one per Pd atom); however, it was later found that additives such as charcoal, $Sn(OAc)_2$, $P(C_6H_5)_3$, and $P(OC_2H_5)_3$ rendered the reaction catalytic (*10, 11*).

The acetoxylation reaction has been the subject of substantial mechanistic conjecture. It was first thought to be a stoichiometric reaction (*8, 9*), then an homogeneous catalyzed free radical reaction (*12, 13*), and subsequently a homogeneous molecular reaction (*14*). More recent work involving the use of palladium phenanthroline complexes suggested that the acetoxylation reaction was actually heterogeneous in nature (*15, 16*). This led us to reexamine the previous systems based on homogeneous catalytic systems involving palladium (II) acetate. The acetoxylation reaction was found to be a purely heterogeneous reaction which occurred on supported metallic palladium particles or on suspended palladium particles in the absence of a carrier material (*7*). The *in situ* prepared, optimized heterogeneous catalysts system, [$Pd(OAc)_2$, $Sn(Octoate)_2$, KOAc, and charcoal] in a Pd/Sn/K mole ratio of 1/5/10 was found to afford 77% selectivity to benzyl acetate at 100% toluene conversion in acetic acid after 180 min at 100°C (*7*). This reaction is particularly sensitive to the stirring rate, which directly influences the exchange between gas-phase oxygen and the liquid/solid catalytic medium.

The preparation of *ex situ* Pd/charcoal catalysts have now been undertaken with the objective of attaining a greater degree of control of the Pd particle size and distribution. Although the *in situ* prepared catalyst system described in (*7*) has lead to substantial gains in selectivity and activity, it was believed that a more rigorous control of the palladium particle size could afford additional improvements. The effects of oxygen pressure, of oxygen pretreatment, and of Sn (II) addition on catalytic activity were also examined. The different rates of acetoxylation of the MAH substrates as a function of steric hindrance and electron-donating groups suggest that the substrate molecule is not directly reacted at the methyl group, but rather adsorbs via formation of Pd_x–π–MAH surface complexes before undergoing oxidative substitution.

METHODS

Catalyst Preparation

Catalysts composed of 3%wt palladium supported on Norit PKDA 1-3 charcoal (10×30 mesh) have been prepared by four different methods to determine the importance of particle size on catalytic activity. The four methods are abbreviated as follows: LPRH (liquid-phase reduction by hypophosphite), LPRF (liquid-phase reduction by formaldehyde), WIHR (wet impregnation and hydrogen reduction), and IEHR (ion exchange and hydrogen reduction).

Norit PKDA 1-3 charcoal has been previously found to be effective as a carrier material for the acetoxylation of MAHs (*7, 10, 11*). The properties of the untreated peat charcoal are as follows: surface area 999 m^2/g, apparent density 0.26 g/cm^3, ash content (7%), total porous volume 1.4 ml/g, grain size: >1.0 mm (86%), >1.7 mm (43%), >2.4 mm (21%). X-ray fluorescence analysis of the ash revealed the major components (other than oxygen) to be Ca 22%, Mg 10%, Si 10%, Al 6%, S 5%, Fe 3%, K 1%, and P 0.7%. All other impurities were below 0.5%. The residual potassium content of the charcoal is substantially inferior to that required for maximum catalytic activity (approximately 11.5% K based on the weight of charcoal used in the experiments). Strong acid treatment of the charcoal carrier (described below) lowered the ash content to 2.6%. The major impurities in the remaining ash were: Si 39%, Mg 4%, Al 4%, Fe 3% and Ca 2%. Strong acid treatment had little effect on the surface area of the support (975 m^2/g).

Preparation of oxidized charcoals. Concentrated nitric acid (250 ml, 67%wt) was added slowly to a 500-ml, round-bottomed flask equipped with a reflux condenser and containing 25 g of Norit charcoal. Nitrogen oxides release was identified by the appearance of significant quantities of red-brown NO_2 vapors. After the gaseous coloration had completely subsided, either (1) the charcoal was filtered off and washed with copious amounts (4 liters) of distilled water (WO, weakly oxidized), (2) the mixture heated for 1 h at 85°C (MO, moderately oxidized), or (3) the mixture was heated for 3 h at 85°C (SO, strongly oxidized). The latter two charcoals were then cooled, filtered, and washed with copious amounts of distilled water (*17, 18*).

The three samples, WO, MO, and SO charcoal, were used as support materials, in addition to nonoxidized (NO) charcoal, for the preparation of different particle size 3%wt Pd/charcoal catalysts. The abbreviations WO, MO, SO, and NO are used as simple notations and are not meant to indicate the amount of surface carboxylation or acidity of the support.

Liquid-phase reduction by hypophosphite, LPRH. A red-brown solution of H_2PdCl_4 was prepared by stirring a suspension of 0.516 g of $PdCl_2$ (2.91 mmol) in 15 ml of 0.2 *M* HCl for 0.5 h. The pH of this solution was adjusted to 7.0 by first adding 0.342 g of NaCl (5.85 mmol), then adding dropwise over a period of 25 min a solution of 5%wt NaOH. The Na_2PdCl_4 solution was discarded if precipitation occurred (*19, 20*).

This solution was then added with vigorous stirring to a suspension of 10 g of the Norit charcoal in 80 ml of distilled water at ambient temperature. Agitation was continued and, after 25 min, 12 ml of a solution of 5%wt sodium hypophosphite (NaH_2PO_2) was added. After an additional 0.5 h of stirring, the catalytic material was recovered by filtration and washed with several consecutive additions of 250 ml of distilled water. Approximately 3 liters of water were used before total absence of chloride ion was assured. A negative cloud point test upon treatment with $AgNO_3$ was obtained after approximately 1.5 liters of water had been passed over the solid. (Note: it has been previously shown that the presence of chloride ion is severely detrimental to catalytic activity (*7*).)

The washed catalyst was then dried for 3 h under reduced pressure (10^{-3} Torr) at 70°C then stored under argon.

Liquid-phase reduction by formaldehyde, LPRF. The Norit charcoal (15 g) was pretreated by stirring for 2 h in the presence of 1 *M* HCl (150 ml) at 50–60°C. The charcoal was subsequently filtered off, then rinsed with a sufficient quantity of water to ensure the absence of chloride ion elution by the $AgNO_3$ cloud point test, see above.

The pretreated charcoal was stirred in 195 ml of water at 95°C and contacted with 4.8 g of Na_2CO_3 (45 mmol) to attain a pH of 9–10. The mixture was then allowed to cool to ambient temperature before adding dropwise, and under continuous agitation, a solution of H_2PdCl_4 (4.4 mmol). The latter solution was prepared by mixing 0.774 g of $PdCl_2$ with 4 ml of 12 M HCl and 5 ml of distilled water. The charcoal and palladium mixture was subsequently heated and maintained at 90°C for 0.5 h. The stirred mixture was then cooled to 75°C and treated by dropwise addition of 3 ml of a solution of 37%wt formaldehyde (32 mmol).

After this series of steps, the temperature of the mixture was again increased to 95°C for 0.5 h before cooling to 60°C and filtering off the catalyst. The material was again washed, dried and stored as indicated above (*19, 20*).

Wet impregnation and hydrogen reduction, WIHR. To a suspension of 10 g of "moderately oxidized" Norit charcoal in 80 ml of distilled water was added 60 ml of H_2PdCl_4 solution, 0.516 g of $PdCl_2$ (2.91 mmol) in 60 ml of 0.2 *M* HCl. The reaction mixture was vigorously stirred for 70 min at ambient temperature then allowed to stand for 65 h. The solid was then filtered off and washed with distilled water until a negative $AgNO_3$ cloud point test indicated the absence of chloride ion elution.

The catalytic material was dried for 3 h at 70°C under reduced pressure, allowed to cool to room temperature, and then transferred to a Pyrex tube. The system was purged with a flow of argon (150 ml/min) for 0.5 h while heating at 50°C. After again cooling to ambient temperature, an $H_2:He$ (20 ml/min : 130 ml/min) gas mixture was initiated and the system heated to 50°C (2.5°C/min). A flow of pure hydrogen (150 ml/min) was then substituted for the mixture and the temperature maintained for 2 h before cooling (*19*).

Ion exchange and hydrogen reduction, IEHR. An aqueous solution (20 ml) of 0.71 g of $[Pd(NH_3)_4]Cl_2$ (2.90 mmol) was added to a suspension of Norit charcoal (10 g) in 100 ml of distilled water with vigorous stirring. Stirring continued for 1 h before the mixture was allowed to stand. After 100 h, the solid was filtered off and treated in a manner identical to the catalyst prepared by the WIHR method (*17–19*).

Catalyst Testing

The operating procedure for the acetoxylation reactions has been previously described (*7*). The experimental apparatus permitted the continuous monitoring of oxygen uptake. All experiments were carried out in a 25-ml Schlenck tube (15 mm i.d.) containing a stirring bar (25 mm by 6 mm) and using a fixed stirring speed of 650 rpm. The Schlenck tube, connected to the experimental assembly, was consecutively charged with 4 ml of 100% acetic acid, 735 mg of 3%wt Pd(0)/charcoal catalyst (i.e. 0.21 mmol of Pd) and 206 mg of potassium acetate (2.1 mmol). The reactor was then charged with the required amount of tin compound, in the form of $Sn(2\text{-ethylhexanoate})_2$ referred to as $Sn(Octoate)_2$, (0.21 to 2.1 mmol) in 1.1 ml (10.35 mmol) of MAH. Toluene served as the reference MAH compound. Immediately after adding the MAH, the tube was flushed with pure oxygen, stoppered, and then pressurized with pure oxygen (generally 1.2 bar absolute). The tube was plunged into an oil bath which had been preheated to the reaction temperature, 100°C.

The only detectable products in the catalytic tests with toluene are benzyl acetate, benzyl diacetate, and benzaldehyde. No benzene was formed. The oxygen balance, oxygen consumption, calculated at the end of the experimental runs is always slightly in excess of the quantity of oxygen required for the formation of the products. The oxygen balance was calculated based on $\frac{1}{2}O_2$ per benzyl acetate and 1 O_2 per benzyl diacetate and 1 O_2 per benzaldehyde, i.e., it was assumed that benzaldehyde resulted from the hydrolysis of benzyl diacetate and thus no additional oxygen was required. The amount of oxygen in excess of stoichiometry (2–4%) was extremely small.

Product and Catalyst Characterization

The reaction products formed by the palladium catalyzed acetoxylation reaction were identified by GC-MS using a 10% FFAP fused silica capillary column (25 m by 0.3 mm i.d.). Quantitative analysis of the products by GC was made possible using *t*-butylbenzene and 1-nitropropane internal standards. The GC analyses were achieved with a 10% FFAP on chromasorb WAW 80–100 mesh column (2 m by $\frac{1}{8}$ in) using a flame ionization detector.

X-ray photoelectron spectroscopic (XPS) analyses were performed on a Kratos

XSAM800 spectrometer using an aluminum cathode (1486.6 eV) as the X-ray source. The samples used in catalytic runs were prepared as described (*7*). Conventional transmission electron microscopic (TEM) analyses were performed using a JEOL 120CX at 100 kV. Samples were transferred to the TEM apparatus without special precaution.

CO chemisorption. Ambient temperature CO chemisorption was performed on a Gira *X*sorb apparatus. All samples (0.9 to 1.4 g) were pretreated under a flow of hydrogen (20 ml/min) for 2 h at 50°C then purged with He gas (20 ml/min) for 2 h before initiating CO pulsing. Pulses of 1 ml were injected at intervals of 4 min until CO adsorption was terminated.

The palladium dispersion (D_{Pd}), the number of surface Pd atoms per gram of catalyst (n_s), the average surface area of metallic Pd per gram of catalyst (S_{Pd}, in m^2/g), and the average Pd particle diameter (Φ_{Pd}, in nm) were obtained using the formulae (*19, 21*)

$$D_{Pd} = n_s/n_t \tag{5}$$

$$n_s = (V_{CO} \cdot N \cdot X_m)/V_M \tag{6}$$

$$S_{Pd} = n_s/s \tag{7}$$

$$\begin{aligned}\Phi_{Pd} &= 6V_{Pd}/S_{Pd}\\ &= [6 \cdot (\%\text{wt Pd}) \times 10^7]/(S_{Pd} \cdot \rho),\end{aligned} \tag{8}$$

where n_t, V_{CO}, s, N, V_M, X_m, V_{Pd}, and ρ represent, respectively, the total number of Pd atoms in one gram of catalyst, the volume of CO adsorbed in cm^3/g, the number of palladium atoms per m^2 (1.27×10^{19}) (*22*), Avogadro's number, the molar volume of CO (approx. 24,000 cm^3/mol at 20°C), the surface Pd-to-CO atomic ratio, the total volume of (cubic) palladium per gram of catalyst, and the density of palladium (1.20×10^5 g/m^3). The only independent variables are V_{CO} and X_m, the former being determined experimentally and the latter estimated to be 1.5.

The value of X_m is very close to 1 when the Pd dispersion is high (*23*). However, preliminary CO chemisorption experiments indicated that the metal was poorly dispersed. Low dispersion favors bridged CO (Pd/CO = 2) over linear CO (Pd/CO = 1). Techniques, such as infrared spectroscopy, have shown that these types of solids may possess as much bridged as linear CO (*23–25*).

RESULTS

The catalysts which have been used in this work were prepared by known literature methods affording a large diversity in palladium dispersion (*17–20*). Our objective is not to study the synthetic techniques which have been previously employed, but rather the catalytic effects resulting from the different materials. Charcoal has been employed as a carrier material in order to provide directly comparative information with the substantial body of scientific work relating to the acetoxylation reaction; see Ref. (*7*) for a review of this subject.

The exact chemical nature of the surface of the Norit charcoal after the oxidation treatments has not been studied; however, the presence of acidic surface oxides on carbon supports has been extensively documented, see for example (*26–29*) and references within. Additionally, the treatment of carbon supports with nitric acid has been previously employed, see for example (*17–19, 29*). The use of nitric acid, at concentrations of 2 *M* or above, leads to the oxidation of significant amounts of surface –OH and carbonyl functions to generate –COOH groups. The concentration of oxygen in top atomic layers of activated carbons has been shown (by XPS) to decrease when raw materials were treated with dilute acid (1 *M* HCl or HNO_3) then increase with stronger acid treatment. It has also been shown that the Pd dispersion increases with increasing concentration of surface oxidic groups (*29*).

Palladium Particle Size

A series of 3%wt Pd on charcoal catalysts were prepared with dispersions over the range of 0.19 to 0.53. The catalytic materials were then tested for toluene ace-

TABLE 1

Influence of the Palladium Dispersion on the Toluene Conversion[a]

Catalysts[b] (3 %wt Pd on charcoal)	V_{CO} (cm^3/g)	D_{Pd}	S_{Pd} (m^2/g)	Φ_{Pd} (nm)	Toluene conversion (%)	Selectivity (%)	
						$PhCH_2OAc$	$PhCH(OAc)_2$
LPRF/MO	0.83	0.19	2.5	5.3	28	83	11
LPRF2/WO	1.14	0.25	3.4	3.9	66	84	12
LPRH/NO	1.20	0.29	3.8	3.4	78	80	15
LPRF/NO	1.46	0.32	4.3	3.1	88	77	18
LPRF/WO	1.47	0.33	4.4	3.0	90	76	18
IEHR/NO	1.73	0.38	5.2	2.5	71	79	15.5
IEHR/NO	1.96	0.43	5.8	2.2	51	81	15
WIHR/MO	2.07	0.46	6.2	2.0	18	83	13.5
IEHR/SO	2.36	0.52	7.0	1.9	5.5	88	10
IEHR/SO	2.38	0.53	7.1	1.9	5	89	8

[a] Reaction conditions: T = 100°C; P_{O_2} = 1.2 bar; reaction time 300 min. Catalytic tests were performed with Pd/charcoal catalysts and with a Pd/Sn/K mole ratio of 1/5/10.

[b] LPRF, liquid-phase reduction (of palladium) by formaldehyde; LPRF2, liquid-phase reduction with a large excess of formaldehyde and a longer reduction step (2 h); LPRH, liquid-phase reduction (of palladium) by hypophosphite; IEHR, ion exchange and hydrogen reduction; WIHR, wet impregnation and hydrogen reduction; NO, WO, MO, SO: non-, weakly, moderately, and strongly oxidized Norit Charcoal.

toxylation activity for 300 min at 100°C. A strong correlation between Pd dispersion and toluene conversion indicated that a dispersion of approximately 0.33 is optimum for this reaction, Table 1. The plot of toluene conversion (catalyst activity) as a function of the volume of CO chemisorbed per gram of catalyst shows the sharp dependence of catalyst activity on the palladium dispersion, Fig. 1. This dispersion corresponds to a Pd particle size of 30–35 Å. The shape of this curve indicates a strict correlation to particle size with no deviation which could be attributed to a variation in

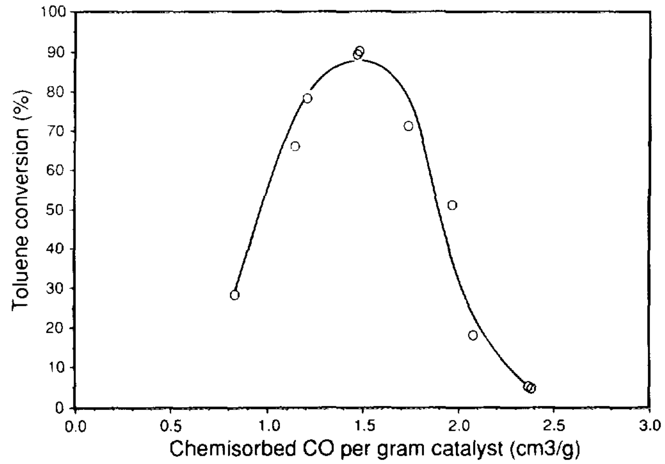


FIG. 1. Toluene conversion as a function of the volume of carbon monoxide chemisorbed per gram of catalyst.

the catalyst preparation method or the support pretreatment.

The presence of chloride ion had been previously found to be detrimental to catalytic activity (*7*). Thus, the appreciable catalytic activity obtained with this system suggests that little or no chloride is present at the catalytically active site, although some strongly bound chloride may reside uniquely on the support.

TEM analysis of the LPRF/WO catalyst was carried out to verify the average Pd particle size estimated by CO chemisorption experiments and to obtain information on the variation in particle size of the sample. Electron micrographs of three regions of this catalyst are shown in Fig. 2. Some regions contain a few Pd particles which appear to be substantially larger than the norm, Fig. 2a, although this may be due to several particles in close proximity. In general, the catalyst is uniform with a very narrow particle size distribution, estimated to be between 20 to 40 Å, Fig. 2b. Other zones contain high concentrations of Pd particles, Fig. 2c. In the latter regions, the particle size is in the 20 to 40 Å range, but the particles are significantly more closely packed, see inset.

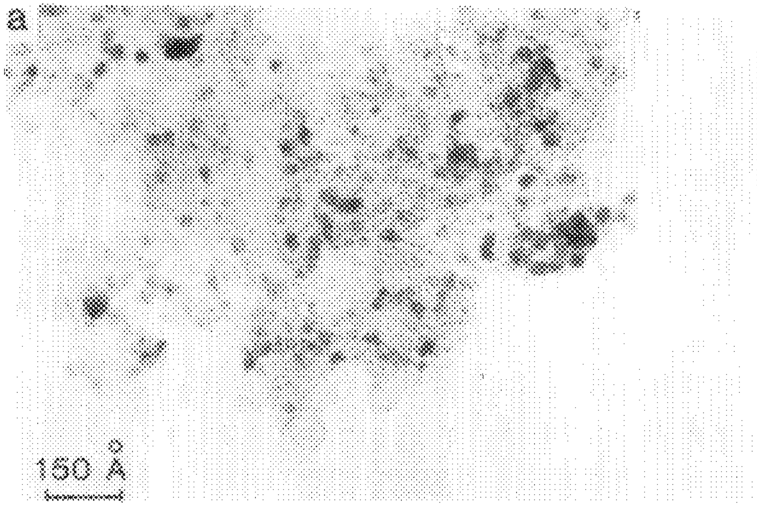
Catalyst Activity

The catalyst found to have the highest activity (LPRF/WO) was studied in more detail. The per cent product yields and unconverted toluene were followed during palladium catalyzed toluene acetoxylation. Fig. 3. After 300 min, the toluene conversion had reached 90% and the yield to the primary product, benzyl acetate, attained a plateau of 69%.

The selectivities toward benzyl acetate and benzyl diacetate are relatively invariant at toluene conversions lower than 65%, Fig. 4. The appearance of benzyl diacetate at low toluene conversion is a confirmation of its formation as a primary product (i.e., it is formed before benzyl acetate desorbs from the catalyst surface); it is also formed as a secondary product after readsorption of benzyl acetate at higher toluene conversion. Benzaldehyde, a secondary product resulting from the hydrolysis of benzyl diacetate, is not formed in significant quantities before about 45% toluene conversion. Above 65% toluene conversion, the selectivities of both diacetate and benzaldehyde increase at the expense of benzyl acetate. These results are in agreement with those obtained using *in situ* prepared catalysts (*7*).

Effect of added tin. The addition of a tin (II) carboxylate to the *in situ* prepared catalytic systems was found to have a major influence on catalytic activity (*7*). This was attributed to at least one major factor: Sn (II) reduces cationic Pd species to metallic palladium. It was shown that induction times for catalytic acetoxylation reactions in the presence of soluble palladium compounds is directly related to the formation of palladium particles. If this was the only role for tin, it would be unnecessary for *ex situ* prepared catalysts in which Pd already exists in metallic form. The effect of the amount of added Sn(Octoate)$_2$ on the activity of the LPRF/WO catalyst was therefore investigated.

The comparative activities of *in situ* and *ex situ* catalyst systems, both with Pd/K ratios of 10, are shown in Fig. 5. The *in situ* catalyst was composed of Pd(OAc)$_2$, Sn(Octoate)$_2$, KOAc, and Norit charcoal. This system involves the addition of Pd(OAc)$_2$ to the reactor immediately before addition of Sn(Octoate)$_2$ and toluene (*7*). The experimental results were obtained after different reaction times, 170 min for the *in situ* system and 200 min for the *ex situ* system; however, this difference in time does not change the appearance of the curve. The toluene conversion for the *ex situ* system with a Sn/Pd mole ratio of 1.5 after 170 min has been indicated to serve as a reference. These results indicate that the addition of Sn(II) to the *ex situ* prepared system has a significantly attenuated influence on catalytic activity. In the absence of Sn (II), the *in situ* system is virtually inac-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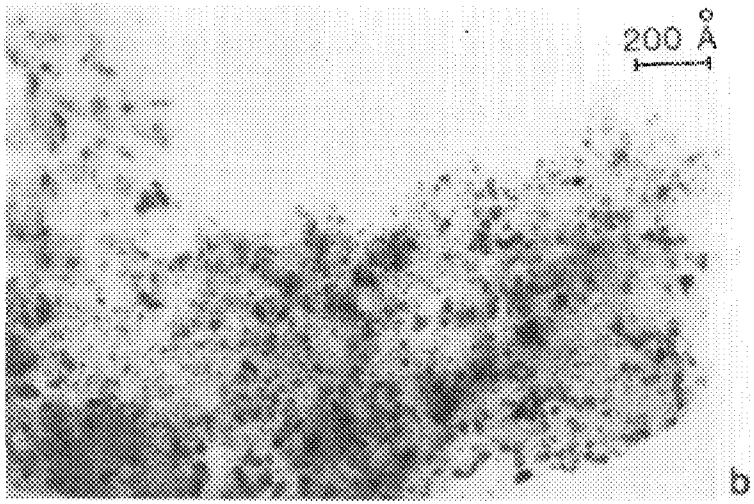
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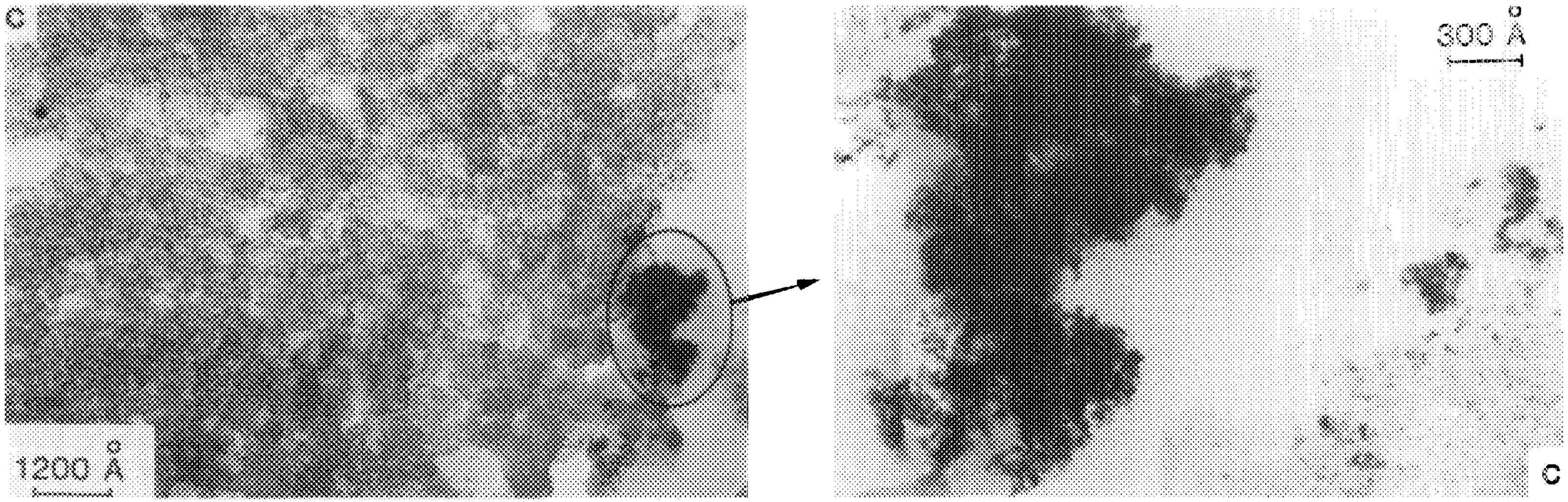
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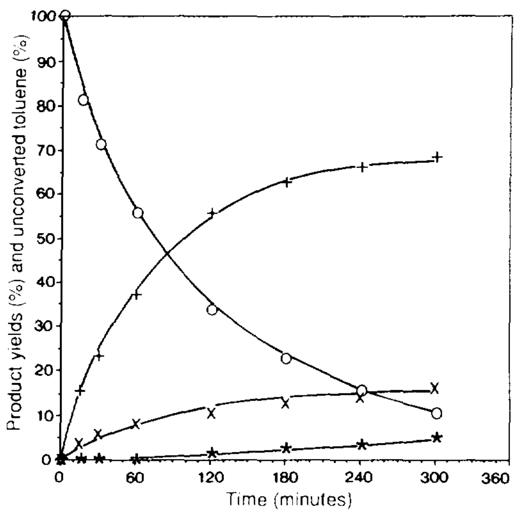

FIG. 3. Product yields and toluene conversion as a function of reaction time: (O) toluene conversion, (+) benzyl acetate yield, (×) benzyl diacetate yield, and (*) benzaldehyde yield.

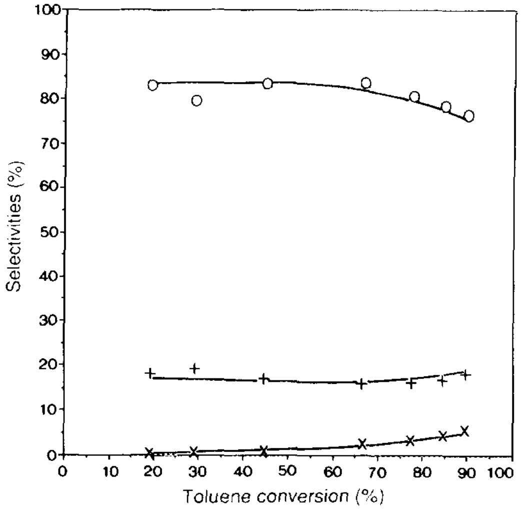

FIG. 4. Product selectivities as a function of toluene conversion: (O) benzyl acetate selectivity, (+) benzyl diacetate selectivity, and (×) benzaldehyde selectivity.

tive; whereas, the *ex situ* system is at about 75% of its maximum activity, i.e., with respect to a Sn/Pd mol ratio of 5.

The *ex situ* system continues to be more active than the *in situ* system up to a Sn/Pd ratio of 2 where the activities become reversed. The *in situ* system is at least 10% more active at an Sn/Pd ratio of 5. It was expected that a well prepared *ex situ* catalyst would be significantly better than the *in situ* counterpart due to the more readily controlled particle size and distribution (*ex situ* = 30–35 Å; *in situ* = 20–100 Å (*7*)). This was not found experimentally over the entire range of Sn-to-Pd ratios for reasons which are not clear.

Effect of oxygen pretreatment. XPS analyses of the LPRF/WO catalyst after catalytic testing for 300 min, either in the presence or the absence of 1.5 equivalents of added Sn(Octoate)$_2$, indicate that Pd is present only in the metallic state. The $3d_{5/2}$ (335.0 eV) and $3d_{3/2}$ (340.3 eV) binding energies are indistinguishable from those of a sample treated under H_2 at 200°C in the XPS pretreatment chamber, corresponding to literature values for metallic Pd (*30*). Identical results were found for the *in situ* prepared catalysts (*7*). Analysis of the tin region of the catalyst containing a Sn/Pd mole ratio of 1.5 yielded the same results as previously obtained, $3d_{5/2}$ = 487.4 eV and $3d_{5/2}$ = 487.4 eV (*7*). This was attributed to either Sn^{2+} or Sn^{4+}. No signal at lower B.E. was observed, thus the presence of Sn^0 is unlikely.

Both *in situ* and *ex situ* prepared systems showed strong inhibition upon increasing oxygen pressure, Table 2. Since the adsorption of hydrocarbon substrates on palla-

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FIG. 2. Electron micrographs of a 3%wt Pd on charcoal catalyst prepared by the LPRF method on WO charcoal: (a) region with some particles larger than 20–40 Å, (b) region with a homogeneous distribution of 20–40 Å particles, (c) region in which the particle size is in the 20–40 Å range, but the distribution is heterogeneous (inset) a dense population of 20–40 Å particles.

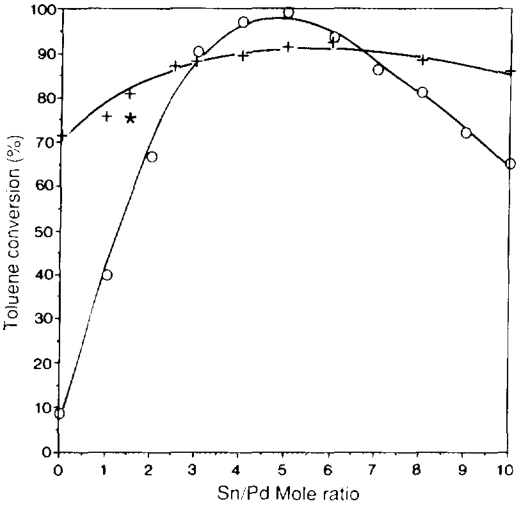

FIG. 5. Variation in the toluene conversion with increasing tin to palladium mole ratio: (○) *in situ* prepared catalytic system for 170 min reaction time, (+) *ex situ* prepared catalyst for 200 min reaction time, and (*) *ex situ* prepared catalyst with a 1.5 Sn to Pd mole ratio after 170 min reaction time (reference).

dium catalysts requires a metal surface, it is logical that as the surface becomes oxidized, reaction rate decreases. In separate *in situ* experiments in which equimolar amounts of palladium and toluene were employed under strictly oxygen-free conditions, 25% of the toluene was converted after 320 min reaction at 100°C and under 1.2 bar of argon. These results suggest that oxygen is not involved in or before the acetoxylation step of the reaction.

The role of oxygen is likely to be to clean the metal surface of hydrogen (hydride) resulting from the rupture of the methyl C–H bond. It has been proposed that the acetoxylation reaction proceeds via (1) the complexation of the aromatic ring with palladium, (2) rupture of a C–H bond of the methyl group to form two fragments, a hydrogen atom (or hydride) and a benzyl radical (or anion), and (3) further reaction yielding water and benzyl acetate (*7*). Thus, an oxygen pressure above that necessary to remove hydrogen from the surface of Pd could lead to oxidation of the Pd surface (formation of PdO) thereby reducing or preventing catalytic activity.

To further test this hypothesis, the LPRF/WO catalyst was preoxidized in the presence of a mixture of 15 vol% O_2 in Ar over different periods of time before contacting the reaction medium, Table 3. Mild preoxidation, 1 h at 100°C, led to a significant loss in catalytic activity (run 2) with respect to the non-oxidized catalyst (run 1). More severe oxidation, 3 h at 200°C, completely shut down catalytic activity. This lost activity can be nearly completely recovered by adding $Sn(Octoate)_2$ during catalytic testing, runs 4 and 5 and Fig. 6. This renewed catalytic activity is explained by the reduction of PdO by Sn(II) to metallic Pd and Sn(IV).

TABLE 2

Influence of the Oxygen Pressure on Toluene Acetoxylation[a]

Catalysts[b]	P_{O_2} (bar)	Time (min)	Toluene conversion (%)	Selectivity (%)	
				$PhCH_2OAc$	$PhCH(OAc)_2$
in Situ[b]	1.2	170	99	78	20.5
in Situ[b]	4	180	70.5	83	16
in Situ[b]	7	330	50.5	87	9.5
LPRH/WO[c]	1.2	210	81	79	16
LPRH/WO[c]	4	240	57	80	14

[a] Reaction conditions, T = 100°C; Pd/Sn/K mole ratio = 1/5/10.

[b] *In Situ* preparation; see Ref. (*17*).

[c] See experimental section.

TABLE 3

Effect of Catalyst Preoxidation on Toluene Acetoxylation Activity[a]

Run	Preoxidation[b]		Sn/Pd (mole ratio)	Reaction time (min)	Toluene conversion (%)
	Time (h)	Temperature (°C)			
1	0	—	0	210	71.5
2	1	100	0	210	25
3	3	200	0	320	0
4	3	200	5[c]	320	68
5	3	200	5[d]	300	82
6	0	—	5	300	90

[a] Reaction conditions: $T = 100°C$; $P_{O_2} = 1.2$ bar; catalyst = LPRF/WO; Pd/K mole ratio 1/10.

[b] Preoxidation of the catalysts was carried out in a tubular reactor using 15 vol% O_2 in Ar (50 ml/min/g).

[c] Sn(Octoate)$_2$ added after 100 min; see Fig. 6.

[d] Sn(Octoate)$_2$ added at reaction time $t = 0$ min.

Acetoxylation of Diverse MAHs

Catalytic systems either prepared by *in situ* or *ex situ* addition of Pd to the charcoal support and with Pd/Sn/K ratios of 1/5/10 have been optimized. Both systems convert toluene at over 90% conversion while maintaining benzyl acetate selectivity at a level of at least 75% (selectivities to benzyl acetate plus benzyl diacetate are in excess of 95%).

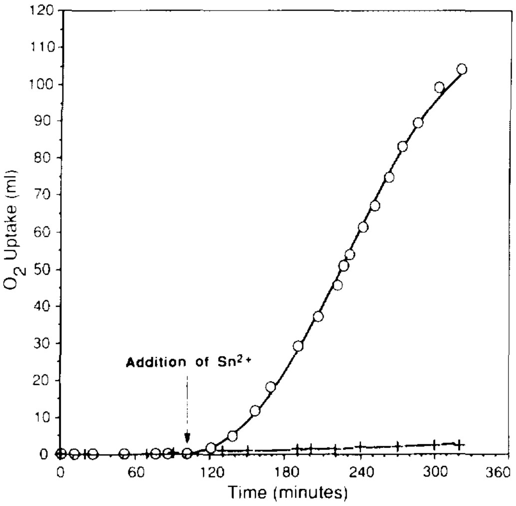

FIG. 6. Variation in total oxygen uptake volume with reaction time (with toluene) for a preoxidized 3%wt Pd LPRF/WO catalyst in the absence of tin: (+) no tin added and (○) the same catalyst in which 5 molar equivalents of tin (with respect to palladium) are added after 100 min.

To increase the possible application of the palladium catalyzed acetoxylation reaction, the reactivities of other MAHs have been investigated. The reactivity of the MAHs shown in Table 4 have been ordered by decreasing relative activity. Although the reaction times are different for the MAHs studied, relative comparisons can be estimated based on the toluene conversion curve shown in Fig. 3.

MAH conversion is noticeably sensitive to the steric bulk on the aromatic ring. The *para*-substitution of toluene by methyl, isopropyl and finally *t*-butyl groups leads to substantial decrease in the rate of reaction. For example, 4-*t*-butyltoluene requires a reaction time at least 42 times longer than that for toluene.

The series of alkoxy-substituted MAHs provides information on the effect of the reaction rate upon addition of resonance effect electron-donating groups to the aromatic ring. The addition of a *para*-methoxy group affords almost the same rate of conversion as toluene. As the substitution approaches the methyl group, meta then ortho

TABLE 4

Catalytic Acetoxylation of Diverse MAHs[a]

MAH	Catalytic systems[b]	Time (min)	MAH conversion (%)	Selectivity (%)[c]	
				Mono-acetate	Diacetate
Toluene	I	210	91.5	77	19.5
	I	10	10	91	8
Toluene	II	170	99	78	20.5
	II	10	10	92	7.5
4-Methoxytoluene	I	230	85	96	2
	II	175	97	96	3
p-Xylene	I	180	75	69	25(1,4) 4(1,1)
o-Xylene	I	235	66	66	29(1,2) 3(1,1)
3,4-Dimethoxytoluene	II	425	55	96	nd
	II	260	31	95	nd
3-Methoxytoluene	II	260	19	98	nd
Ethylbenzene	I	240	12	80(Cα)	[d]
4-Methylacetophenone	II	300	21	97	nd
Benzyl acetate	II	285	15	—	89[e]
2-Methylnaphthalene	II	345	18	96	nd
	II	150	10	98	nd
3,4-(Methylenedioxy) toluene	II	425	16	97	—
4-Isopropyltoluene	II	320	11	97	nd
2-Methoxytoluene	II	330	11	97	nd
Mesitylene	I	320	9	93	nd
4-Chlorotoluene	II	330	7	98	nd
4-*t*-Butyltoluene	I	410	8	97	nd
	II	420	9	96	nd
4-Nitrotoluene	II	330	2	99	nd
3-Phenoxytoluene	II	330	0	—	—

[a] Reaction conditions: $T = 100°C$, $P_{O_2} = 1.2$ bar.

[b] I = LPRF/WO, II = *in situ;* Pd/Sn/K mole ratio = 1/5/10.

[c] nd = not determined; numbers or letters in parentheses indicate substitution position.

[d] In addition to the α-Methylbenzyl acetate, 5% styrene, 3% styryl acetate, 12% other products.

[e] Benzaldehyde selectivity = 11%.

substitution, the reaction rate decreases. If the reaction were not governed by steric factors, *ortho* substitution would have been expected to afford a higher rate of reaction than meta. Steric encumberance at the *meta* and *para* positions reduce the adsorption interaction between the aromatic ring and the Pd surface; on the other hand, steric hindrance at the ortho position effects activation of the methyl C–H bond.

As the steric effect of 4-methoxytoluene was limited, 3,4-dimethoxytoluene was examined. Its activity was found to be in between the para and meta-substituted toluenes. This result confirms that the addition of a nonsterically demanding group which is electron-donating by the resonance effect is more favorable for the reaction rate than the addition of an alkyl group.

The reaction rate of 3,4-(methylenedioxy)toluene is substantially lower than that for 3,4-dimethoxytoluene. The locked position of the methylene group blocks adsorption from one side of the ring thereby lowering the probability of adsorption. *Meta*-phenoxytoluene is completely inactive. This is believed to be due to two factors: first, the requirement to rotate the phenoxy-group to an exo-surface orientation and second, upon eventual adsorption of the first aromatic ring, the phenoxy aromatic ring will also adsorb creating a very strong substrate–surface interaction. A similar strong interaction has been postulated for the very low activity found during competition experiments in which naphthalene was present *vide infra*.

The presence of electron-withdrawing groups at the para position has a strongly adverse effect. Catalytic acetoxylation activity was found to decrease with increasing force of the electron acceptor group on the MAH *para* position: activity MeCO > Cl > NO_2.

Toluene Acetoxylation Competition Studies

The relatively large size of the Pd particles required for the acetoxylation of MAHs (30–35 Å) has been suggested to be due to the need to adsorb the MAH aromatic ring before reaction of the methyl group (*7*). Competition experiments between toluene and various hydrocarbons were undertaken to attempt to provide experimental evidence which could corroborate this adsorption requirement, Table 5.

TABLE 5

Competition Experiments between Toluene and Others Substrates[a]

Run	Competitor substrate	Time (min)	Toluene conversion (%)
1	Ethylcyclohexane	120	79
2	4-*t*-Butyltoluene	120	80.5
3	4-Chlorotoluene	120	78.5
4[b]	Ethylcyclohexane	120	53
5[b]	Benzene	120	35.5
6	Ethylcyclohexane	170	99
7	Methoxybenzene	170	77
8	Naphthalene	170	10

[a] Reaction conditions: $T = 100°C$, $P_{O_2} = 1.2$ bar, *in situ* catalyst system, Pd/Sn/K mole ratio 1/5/10, 15 mol% toluene replaced by the competitor substrate.

[b] Experiments carried out at 80°C.

Ethylcyclohexane was chosen as a spectator substrate due to its complete inactivity, lack of an aromatic ring, boiling point and chromatographic retention time which did not interfere with the characterization of the products. The experiments were carried out using standard protocol except that 15 mol% toluene was replaced by an equivalent amount of the competitor substrate. Two experiments were performed at 80°C (tests 4 and 5), one with ethylcyclohexane and one with benzene. This lower temperature was employed to assure that benzene would remain in the liquid phase.

After 120 min, pure toluene is converted at a level of 83% (*7*). Toluene conversions in the presence of 15 mol% ethylcyclohexane (spectator substrate, test 1), 4-*t*-butyltoluene (sterically hindered MAH, test 2) or 4-chlorotoluene (electron accepting substituted MAH, test 3) are within 2% conversion of each other (78.5–80.5), indicating that these substrates do not compete with toluene for the active sites on the catalyst surface.

The comparison between tests 4 and 5 clearly show that benzene has a negative effect on catalyst activity, lowering toluene conversion by 33% with respect to dilution with ethylcyclohexane. It was thus concluded that benzene adsorbs onto the same sites as toluene. Similarly, methoxybenzene (electron donating aromatic hydrocarbon, test 7) lowers toluene conversion by 33% with respect to an experiment with the spectator substrate (test 6). Neither benzene nor methoxybenzene is chemically reactive in the reaction medium.

Finally, the addition of naphthalene (test 8) reduces toluene conversion by 90%, indicating that naphthalene is very strongly adsorbed to the surface. These results demonstrate that the adsorption of the aromatic ring of the MAH is a requirement for reactivity at the methyl group.

DISCUSSION

The reaction steps proposed for the palladium catalyzed acetoxylation of methylated aromatic hydrocarbons (MAHs) are considered to be the most consistent with the information contained in this work and a previous study (7); see Eqs. (9)–(15) and Fig. 7. The initial step appears to be the adsorption of the electron-donating substrate molecule onto palladium particles, Eq. (9). Slightly positively charged (i.e., electron-poor) palladium would be expected to have a higher affinity for the electron-donating substrate than neutral or negatively charged palladium. It may be that the *in situ* prepared catalyst is more active than the well-defined *ex situ* system due to the encapsulation of potassium ion (6-fold ionic radius, 1.38 Å) by palladium (12-fold metallic radius, 1.37 Å) during particle formation. This would render the particles more electro-positive and thus increase their affinity for electron-rich substrates. The decoration of Sn around the Pd particles may also vary with preparation. Either one or both of these factors are likely to be associated with the difference in activity.

The second step in the acetoxylation mechanism is proposed to be the rupture of the methyl C–H bond to form benzyl–Pd and H–Pd surface species, Eq. (10). We have chosen to represent these species as radical fragments rather than as charged species to eliminate confusion and unnecessary conjecture.

The primary product results from reaction of the adsorbed benzyl fragment with acetate ion, Eq. (11). This processus releases an electron to the palladium particle. Equations (10) and (11) have been represented as individual reaction steps; however, there appears to be no reason for not considering them as a single concerted step; see Fig. 7. A concerted palladium-assisted S_N2 mechanism could be viewed as the simultaneous addition of an acetate ion and the release of a hydride to the Pd sur-

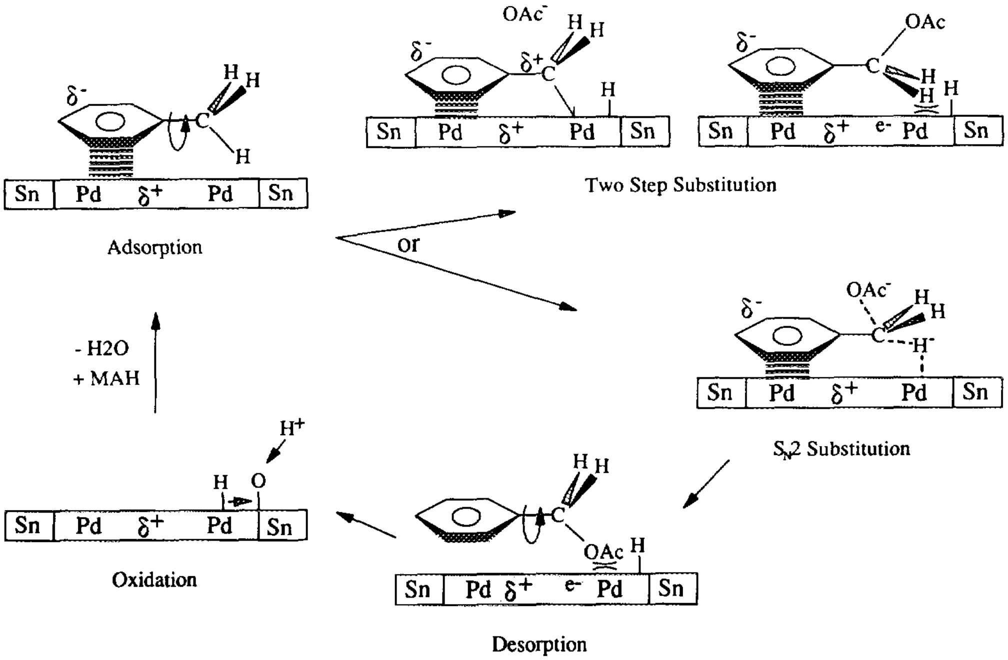

FIG. 7. Schematic representation of some of the proposed steps involved in methylated aromatic hydrocarbon acetoxylation. Shown are the adsorption (Eq. (9)), desorption (Eq. (12)) and oxidation steps (Eq. (15)), and the possible mechanisms for substitution: two step (Eqs. (10, 11)) or S_N2. Not shown is the oxygen chemisorption step (Eq. 14)).

face. It is likely that one of these steps or the MAH adsorption equilibrium (Eq. (9)) is the rate determining step. The formation of secondary products, such as benzyl diacetate, would be expected to be more important if the product desorption equilibrium (Eq. (12)) was rate-determining:

$$RH_{(l)} \rightleftharpoons RH_{(ads)} \tag{9}$$

$$RH_{(ads)} \rightleftharpoons R_{(ads)} + H_{(ads)} \tag{10}$$

$$R_{(ads)} + AcO^-_{(l)} \rightarrow ROAc_{(ads)} + e^- \tag{11}$$

$$ROAc_{(ads)} \rightleftharpoons ROAc_{(l)} \tag{12}$$

$$\tfrac{1}{2}O_{2(g)} \rightleftharpoons \tfrac{1}{2}O_{2(l)} \tag{13}$$

$$\tfrac{1}{2}O_{2(l)} \rightarrow O_{(ads)} \tag{14}$$

$$O_{(ads)} + (H_{(ads)} + e^-) + H^+_{(l)} \rightarrow H_2O_{(l)}. \tag{15}$$

The acetoxylation reaction is driven by the exothermic formation of water. Without the addition of oxygen to the reaction medium, the conversion of toluene is limited to 0.25 turnovers per Pd atom, *vide ante*. The oxidation of a clean metal surface (Eq. (14)) and the formation of water on group VIII metals in the presence of surface hydrogen and oxygen are generally very fast reactions, thus unlikely to be rate determining. The latter reaction has been represented as a single step (Eq. (15)) for simplicity. The formation of water is likely to involve protonation of a surface hydroxyl group in this acidic medium. In Eq. (15), a hydrogen atom and an electron have been written on the right side of the reaction to denote either a surface hydride or an adsorbed hydrogen atom and an electron from the palladium particle.

One of the roles of tin during the preparation of the *in situ* catalyst has been described. Cationic palladium (Pd^{2+}) is reduced by Sn^{2+} to generate Pd^0 and Sn^{4+}. It is clear that tin must play an additional role or it would have had no effect on the catalytic activity on the *ex situ* system in which palladium is already in metallic form.

A second role for tin may be to control the amount of oxygen available for water formation. The presence of Sn(IV) oxide, in a decoration environment around the Pd particles, may be reduced in the presence of surface hydride on palladium, Eq. (16). Under oxygen-poor conditions, hydrogen could migrate to the Pd(0)–Sn(IV) oxide interface and form water in the protonated medium. The addition of oxygen to the system would result in the rapid formation of surface PdO. This surface oxygen then migrates to the Pd(0)–Sn(II) interface resulting in the reduction of palladium, Eq. (17):

$$Pd_x - H^- + SnO_2 + H^+ \rightarrow Pd_x + SnO + H_2O \tag{16}$$

$$PdO + SnO \rightarrow Pd + SnO_2. \tag{17}$$

The *ex situ* prepared catalyst system functions in the absence of tin, indicating that tin is not required for catalytic activity for the acetoxylation reaction. However, the addition of tin up to a Sn/Pd ratio of 5 led to an increase in catalytic activity. This supplementary activity resulting from tin addition may reflect the non-steady state operation of the catalytic system (which is probably oxygen-rich at the liquid–gas interface) or perhaps a subtle electronic effect which has not been taken into account.

CONCLUSION

The palladium-catalyzed acetoxylation of MAHs occurs on the surface of supported metallic palladium where the optimum particle size for the acetoxylation of toluene to benzyl acetate has been shown to be 30–35 Å. All of the experimental results are consistent with a preadsorption of the aromatic ring by electron-donation to palladium before activation of the methyl C–H bond.

Interestingly, the selective hydrogenation of 1-butyne, 1,3-butadiene, and isoprene by palladium catalysts have also been reported to be highly dependent on particle size, requiring dispersions of less than about 0.25 (*31*, *32*). It is believed that the large number of Pd atoms required for this reaction is due to an electronic factor. The Pd particles being required to attain a certain level of metallic character before attaining high activity. This may also be important for the benzylic acetoxylation reaction.

Alkali doping of heterogeneous catalysts is known to be extremely important for a number of reactions, such as ethylene oxide, styrene, ammonia, and sulfuric acid synthesis, and the oxychlorination and Fischer–Tropsch reactions (*33*). The "modes of action of the alkali ions" are considered to number at least eight, among which are considered the modification of the electronic properties of the catalyst surface and auxiliary functions during the preparation of the catalyst (*33*).

Potassium ion has an important effect on catalytic activity for both *in situ* and *ex situ* prepared acetoxylation catalysts. K^+ probably renders the Pd particles more electropositive and thereby more susceptible to the addition of an electron-donating substrate. Surprisingly, *in situ* prepared catalysts outperform the more rigorously controlled *ex situ* catalysts. This may be due to the encapsulation of some K^+ into the Pd particles during *in situ* catalyst preparation.

The presence of added tin is suggested to be beneficial for two reasons: (1) Sn(II) permits the reduction of Pd(II) to Pd(0), which is particularly important for *in situ* prepared catalysts, and (2) Sn(IV) oxide serves as an oxygen reservoir during oxygen-poor regimes, permitting the formation of water by the reaction with Pd surface hydrogen at the Pd/Sn interface.

The presence of Sn^0 was not observed in the XPS spectra of diverse samples containing tin. This is perhaps evident in that the samples were neither reduced at high temperature nor used in a reducing atmosphere. It is thus likely that the interaction between palladium and tin in this catalytic system is very different than that for platinum and tin in reforming catalysts. The latter have been shown to exhibit some PtSn alloy formation after reduction at temperatures above 450°C (*34–37*).

To date nearly all reported palladium catalyzed acetoxylation reactions have been carried out in batch reactors at near atmospheric pressure and at 100°C. Two notable exceptions are acetoxylation experiments with toluene and 4-methoxytoluene which were performed under 4 bar of oxygen at 140°C yielding turn over frequencies of 63 and 42 molecules per atom of palladium per hour respectively (*7*). Continuous operation in a tubular, plug-flow reactor in which oxygen is solubilized in the liquid phase under pressure and at higher temperature should lead to greatly improved results. The latter system would not require a controlled agitation rate nor have the problem associated with a gas/liquid interface.

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