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Synthesis of Lactic Acid *via* Palladium-Catalyzed Carbonylation of Vinyl Acetate

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The methoxycarbonylation of vinyl acetate monomer (VAM) was studied with Pd-catalysts at 5.4 MPa CO partial pressure and 373 K. The effects of several acidic and basic ligands in the presence and absence of a promoter were investigated. Using pyridine as ligand in the [$PdCl_2(PPh_3)_2$]-TsOH catalyst system resulted in 90.01% conversion of VAM and 76.12% selectivity for carbonylation products (methyl-2-acetoxypropionate and methyl lactate). The VAM methoxycarbonylation could be facilitated in a non-polar solvent media and produces methyl-2-acetoxypropionate and methyl lactate, which can be easily converted to lactic acid *via* hydrolysis.

Keywords: Methoxycarbonylation, Vinyl acetate monomer, Palladium catalyst, Methyl-2-acetoxypropionate, Methyl lactate.

INTRODUCTION

Lactic acid is used commercially in the pharmaceutical, baking, dairy, pharmaceutical and cosmetic industries, as well as in wool dyeing and the production of resin plasticizers [1,2]. Recently, lactic acid has received special interest because of its application as a building block for biobased polymers [3-5]. The demand has increased due to its role as a precursor in the synthesis of polylactic acid [6]. However, alternative method yielding lactic acid at a low cost of production using environmental friendly methods would result in a dramatic increase in the existing market and the evolution of a range of new applications [7-10]. Current commercial methods for lactic acid synthesis (fermentation of molasses and hydrocyanation of acetaldehyde) produce stoichiometric byproducts, which is undesirable from an economical and environmental point of view. Both commercial processes produce racemic lactic acid, while the resolution is carried out separately since only L-lactic acid is useful in polylactide synthesis [11-13].

A novel catalytic route using vinyl acetate monomer (VAM) (industrially produced in large volumes from ethylene) was proposed for lactic acid synthesis, which deserves consideration [14-16]. A few methods such as rhodium catalyzed hydroformylation followed by oxidation and hydrolysis (75% yield of DL-lactic acid) [17]. The palladium complexes are known to catalyze the carbonylation reactions efficiently [18,19]. For example, the palladium catalyzed hydrocarbonylation (60.3% yield of 2-acetoxy propionate at 373-473 K, 0.6-6.9 MPa) [20] and Pd-catalyzed methoxycarbonylation (62-82% yield of methyl-2-acetoxypropionate at 373-473 K and 7-25 MPa), where lower catalytic activity and selectivity to carbonylation products were reported at severe reaction conditions [21-23]. Despite the fact that carbonylation of VAM is demonstrated to be an essential step in the plausible synthesis of DL-lactic acid, no comprehensive studies have been reported.

This study investigated the methoxycarbonylation of VAM utilizing various palladium catalyst precursors, ligands, promoters and solvents to optimize the catalytic activity and selectivity in order to obtain methyl-2-acetoxypropionate and methyl lactate. The VAM alkoxycarbonylation products were hydrolyzed with a variety of acidic catalysts to produce DL-lactic acid.

EXPERIMENTAL

The chemicals *viz.* $PdCl_2$, $Pd(OAc)_2$, $Pd(acac)_2$, 2,2′,2″-terpyridine, 2,2′-bipyridine, 1,10-phenanthroline, pyridine-2-carboxylic acid, acetyl acetone (acac) and vinyl acetate (VAM) were purchased from Aldrich Chemicals (Milwaukee, USA).

Whereas the solvents *viz.* acetonitrile, methanol, toluene, chlorobenzene, pyridine, anthranilic acid, tetrahydrofuran (THF), tosylic acid (TsOH), triphenylphosphine (PPh_3), tetrabutylammonium chloride hydrate ($TBACl{\cdot}H_2O$), tetrabutylammonium bromide (TBABr), tetrabutylammonium iodide (TBAI), and nicotinic acid were obtained from SD Fine Chemicals (Mumbai, India). Carbon monoxide (99.9% purity) was supplied by Matheson (Montgomeryville, PA, USA). The palladium complexes *viz.* $[PdCl_2(PPh_3)_2]$, $[PdBr_2(PPh_3)_2]$ and $[PdI_2(PPh_3)_2]$-$[PdCl_2(AsPh_3)_2]$ were synthesized as per literature [24].

General procedure for carbonylation reaction: The VAM carbonylation reactions were carried out in 50 mL Parr Autoclave made of Hastelloy-C-276 with digital temperature and pressure display. In a typical VAM carbonylation reaction, toluene (solvent) was added to a known amount of VAM and methanol to make up the volume 25 mL and charged to the reactor. The weighed quantities of $[PdCl_2(PPh_3)_2]$ and other promoters (if specified) were also charged and the reactor was closed. Thereafter, the contents were purged once with nitrogen and thrice with carbon monoxide. The reactor was heated to the desired temperature, which was then pressurized with CO to a desired pressure. The reaction was begun at 16.66 Hz and maintained at a constant pressure by supplying CO from a reservoir through a constant pressure regulator. The CO consumption monitored the reaction's progress as a time function. After the specific time intervals, intermediate samples were taken out for analysis if required. The reaction was continued at constant pressure for a particular time and was then cooled to room temperature. The gas was vented off, the reactor flushed with N_2 and the contents removed. A small volume of liquid sample was removed and GC was used to do a quantitative analysis.

Hydrolysis of carbonylation products: A known amount of methyl-2-acetoxypropionate (isolated from carbonylation reactions) was taken in a 50 mL round bottom flask containing 15 mL distilled water (methyl-2-acetoxypropionate was insoluble in water). Subsequent to the addition of a certain quantity of catalyst, the mixture was heated to 353 K while undergoing agitation. After a specific reaction time, the contents were cooled to room temperature. Unreacted methyl-2-acetoxypropionate was extracted in toluene and measured using GC. When toluene extract was analyzed, only methyl-2-acetoxypropionate and trace lactic acid were isolated. The aqueous phase was found to contain lactic acid, which was characterized using GC-MS. Subsequently, 25 mL of aqueous fraction containing extracted methyl lactate was transferred to 50 mL round-bottom flask. A known amount of catalyst was added and heated at 353 K under stirring. After a specific reaction time, the contents were cooled to room temperature and quantitatively analyzed using GC for methyl lactate.

Characterization: IR analysis was done on Bio Rad FTS 175C spectrophotometer. NMR spectrum was obtained from Brucker- MSL300 and Brucker-AC200 machines. Elemental analysis 125 was carried out on a CHNS-O EA1108, Elemental analyzer of Carlo Erba Instruments. Liquid samples of carbonylation reactions were quantitatively analyzed with HP 6890 GC using HP1 methyl siloxane capillary column (length 30 m, diameter 30 μm, film thickness 0.25 μm). Conditions: Split (50:1) Inlet temperature, 523 K; Column temperature, 303-523 K (programmed); Detector (FID), 523 K; Carrier gas (He) flow, 20 mL/min. The quantitative analysis was obtained through a calibration curve. Conversion of VAM, selectivities to methyl-2-acetoxypropionate, methyl lactate and methyl acetate were calculated.

Isolation and characterization of methyl-2-acetoxypropionate: A series of VAM methoxycarbonylation reactions were carried out at 373 K, using $[PdCl_2(PPh_3)_2]$ as catalyst and the reaction mixtures were collected to isolate the carbonylation product. Toluene (solvent), unreacted components (methanol and VAM) and methyl lactate formed were removed under vacuum at 313 K, which left behind the liquid methyl-2-acetoxypropionate and the precipitated catalyst $PdCl_2(PPh_3)_2$. The catalyst was filtered off; the product was passed through a silica column and eluted with hexane as a solvent to remove any trace of impurities. The isolated product was characterized using IR (ν_{CO} = 1745 cm^{-1}); ^1H NMR (δ, ppm): 5.01 (q, J = 7.05 Hz, 1H), 3.67 (s, 3H), 2.06 (s, 3H), 1.43 (d, J = 7.02 Hz, 3H)] and GC-MS, which is consistent with the literature [23]. The compound was used as a standard for quantitative analysis of methoxycarbonylation reaction mixtures using GC and its hydrolysis to lactic acid.

Extraction of methyl lactate from carbonylation reaction mixtures: Carbonylation reaction mixtures containing methyl-2-acetoxypropionate, methyl lactate, methyl acetate unreacted VAM and solvent (toluene) were collected. Methanol, methyl acetate and VAM were removed using a rotary evaporator at 310 K, while the methyl lactate was extracted in water. The hydrolysis was performed on 0.5% methyl lactate fraction obtained from GC analysis.

RESULTS AND DISCUSSION

The main objective of this work is to study the activity and selectivity of Pd-catalysts for methoxycarbonylation of vinyl acetate monomer (VAM) to carbonylation products methyl-2-acetoxypropionate, followed by hydrolysis of the carbonylation product to DL-lactic acid using acid catalysts. For this purpose, a few experiments were carried out using $PdCl_2(PPh_3)_2$ as catalyst at 373 K and 5.4 MPa CO pressure to identify and characterize the products formed. A typical concentration-time profile for 373 K is shown in Fig. 1.

The main products formed were methyl-2-acetoxypropionate (isolated from the reaction mixture and used as a standard for GC analysis), methyl lactate, methyl acetate and dimethyl acetal as identified by GC and GC-MS. The molar stoichiometric of VAM conversion produce methyl-2-acetoxypropionate (**D**), methyl acetate (**E**), methyl lactate (**F**) and acetaldehyde (**G**). Acetaldehyde (**G**) further reacts with methanol to form dimethyl acetal (**H**) as shown in **Scheme-I**. The converted VAM was observed to be in the range of 91-99% with respect to the products, whereas methanol and CO consumed was observed to be in the range of 96-98 and 80-95%, respectively.

Effect of catalyst precursors: Initially, the catalytic activity of different palladium catalysts was examined (Table-1). It was found that $[PdCl_2(PPh_3)_2]$ was the most effective catalyst for the methoxycarbonylation reaction of VAM giving 99.12%

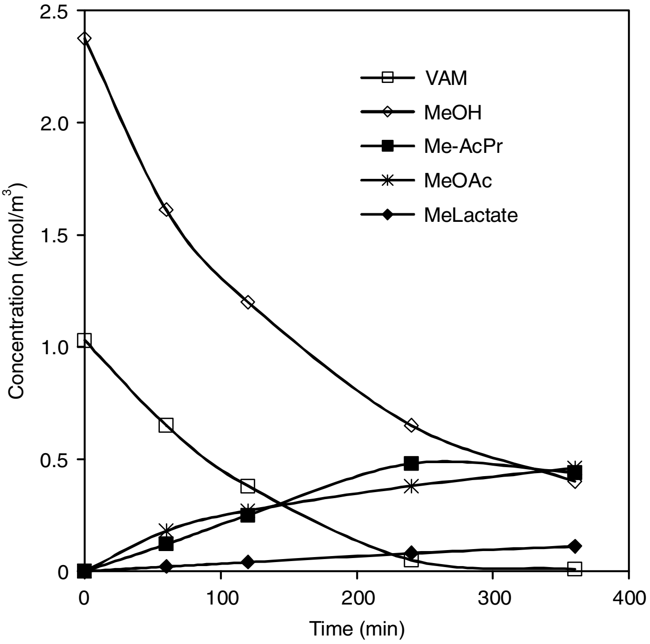
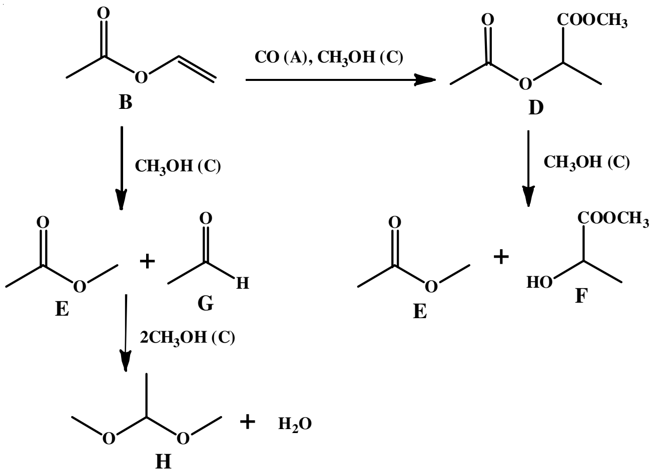


Fig. 1. Concentration-time profile of VAM methoxycarbonylation reaction at 373 K; **Reaction conditions:** $PdCl_2(PPh_3)_2$: 2×10^{-3} kmol/m^3; VAM: 1 kmol/m^3; CH_3OH: 2.4 kmol/m^3; Solvent: toluene; Total volume: 2.5×10^{-5} m^3; Temperature: 373 K; PCO: 5.4 MPa; Agitation speed: 16.66 Hz



Scheme-I: Schematic of reactions involved in methoxycarbonylation of VAM

conversion of VAM with 53.91% combined selectivity to the carbonylation products (Table-1, run# 6) and at the same time, the rest of VAM was converted to methyl acetate. $PdCl_2$ alone gave no reaction whereas the addition of 2 equiv. of PPh_3 as a ligand to $PdCl_2$ showed an activity similar to $[PdCl_2(PPh_3)_2]$ catalyst (Table-1, run# 1[b], 2[c], 6). Similarly, $[PdCl_2Py_2]$ as catalyst showed no carbonylation activity, but the addition of 2 equiv. of PPh_3 to this catalyst showed the activity comparable to $[PdCl_2(PPh_3)_2]$ catalyst (Table-1, run# 3[b], 4[c], 6). Other palladium precursors such as $[PdCl_2(AsPh_3)_2]$, $[Pd(OAc)_2]$, $[Pd(acac)_2]$ were screened for this reaction without PPh_3 ligand which showed no carbonylation activity (Table-1, run# 5[b], 9[b], 10[b]). These catalysts were found deactivated, as a substantial amount of palladium black was observed in the reaction mixtures, where no PPh_3 was used. Palladium was found to be active in the form of $[PdCl_2(PPh_3)_2]$, which was either charged as a prepared complex or formed *in situ* by the addition of PPh_3 ligand to a palladium precursor.

When $[PdX_2(PPh_3)_2]$ (where X = Cl, Br or I) catalysts with various halogen atoms were tested for methoxycarbonylation reaction, the trend in activity ($X = Cl > Br >> I$, in $[PdX_2(PPh_3)_2]$ was similar to reported work of Sugita & coworkers [23] using $[PdX_2(PPh_3)_2]$ as catalyst in the presence of pyridine as ligand at particular operating conditions (373-423 K, 15-25 MPa), but the catalytic activity was very low and the reason is attributed due to the extremely low concentration of VAM (VAM/Pd ratio = 20). In present case, a higher VAM concentration (VAM/Pd ratio = 500) showed 11 times increase in the catalytic activity compared to the literature even in the absence of pyridine ligand at milder reaction conditions [23] (Table-1, run# 6).

Effect of quaternary halides as promoters: Different quaternary ammonium (tetrabutylammonium) halide salts were screened for VAM methoxycarbonylation reaction as promoters along with $[PdCl_2(PPh_3)_2]$ as catalyst, in which it was observed that TBACl was superior among the other ammonium halides. The addition of 20 equiv. of TBACl to $[PdCl_2(PPh_3)_2]$ catalyst showed 63.04% conversion of VAM in 4 h with an improvement in selectivity to carbonylation products (from 53.91 to 62.5%) (Table-2, run # 1 and 2). The use of TBABr as a promoter decreased the catalyst activity towards the carbonylation products (Table-2, run # 3), whereas TBAI as a promoter showed only VAM methylation product, methyl acetate without any

TABLE-1
EFFECT OF PALLADIUM PRECURSORS IN THE CARBONYLATION OF VINYL ACETATE MONOMER (VAM)

Run No.	Catalyst	Time (h)	[a]Conversion (%)	[a]Selectivity (%)			TOF (h^{-1})
				D	E	F	
1[b]	$PdCl_2$	4	6.13	0	50.30	0	0
2[c]	$PdCl_2$	10	98.76	44.13	45.37	10.67	27
3[b]	$[PdCl_2Py_2]$	4	8.96	0	49.67	0	0
4[c]	$[PdCl_2Py_2]$	10	98.05	42.35	47.40	8.43	28
5[b]	$[PdCl_2(AsPh_3)_2]$	4	54.68	0	46.89	0	0
6	$[PdCl_2(PPh_3)_2]$	10	99.12	43.13	45.09	10.78	28
7	$[PdBr_2(PPh_3)_2]$	4	25.28	21.54	51.72	4.33	9
8	$[PdI_2(PPh_3)_2]$	4	12.00	0	72.47	0	0
9[b]	$[Pd(OAc)_2]$	2	3.67	0	44.90	0	0
10[b]	$[Pd(acac)_2]$	2	0.98	0	0	0	0

Reaction conditions: Catalyst: 2×10^{-3} kmol/m^3; VAM: 1 kmol/m^3; Methanol: 2.4 kmol/m^3; Solvent: Toluene; Total Volume: 2.5×10^{-5} m^3; Temperature: 373 K; P_{CO}: 5.4 MPa; D: Methyl-2-acetoxypropionate; E: Methyl acetate; F: Methyl lactate; [a]By GC analysis; [b]Substantial amount of palladium was found precipitated in the reactor when discharged; [c]PPh_3: 4×10^{-3} kmol/m^3

TABLE-2
EFFECT OF QUATERNARY AMMONIUM HALIDES (QX) IN THE CARBONYLATION OF VINYL ACETATE MONOMER (VAM)

No.	Promoter	Time (h)	^{a}Conversion (%)	^{a}Selectivity (%)			TOF (h^{-1})
				D	E	F	
1	–	10	99.12	43.13	45.09	10.78	28
2	TBACl	4	63.04	55.63	37.60	11.87	52
3	TBABr	4	32.05	20.88	57.67	5.86	10
4	TBAI	4	24.02	0	82.47	0	0

Reaction conditions: $[PdCl_2(PPh_3)_2]$: 2 × 10^{-3} kmol/m^3; VAM: 1 kmol/m^3; CH_3OH: 2.4 kmol/m^3; Promoter: 4 × 10^{-2} kmol/m^3; Solvent: Toluene; Total Volume: 2.5 × 10^{-5} m^3; Temperature: 373 K; P_{CO}: 5.4 MPa; Selectivity: D: Methyl-2-acetoxypropionate; E: Methyl acetate; F: Methyl lactate

carbonylation reaction (Table-2, run # 4). Using a promoter TBAX with X = Cl, Br or I, in the presence of $[PdCl_2(PPh_3)_2]$ as a catalyst, a typical trend in the catalyst activity was observed in the order: Cl > Br >> I in TBAX. Though these trends were representative of $PdX_2(PPh_3)_2$ formed, it can be observed that the use of a halide promoter increased the conversion of VAM as well as selectivity to the carbonylation products (Table-2, run # 2, 3 and 4).

Effect of ligands: To increase the selectivity of carbonylation products, various ligands containing N- and O- donor atoms were screened for VAM methoxycarbonylation reaction along with $PdCl_2(PPh_3)_2$ as catalyst in the presence and absence of TsOH. The addition of 4 equiv. of TsOH to $PdCl_2(PPh_3)_2$ catalyst system helped to increase the conversion of VAM in lesser reaction time (99.89% in 4.5 h), but the selectivity to carbonylation products was found to be lowered with an increase in the selectivity to methyl acetate (Table-3, run# 1, 2^b). Further, the addition of 20 equiv. of *N*-donor ligand (basic in nature) to $[PdCl_2(PPh_3)_2]$-TsOH catalyst system enhanced the selectivity of carbonylation products at the cost of conversion. Use of acidic ligands (picolinic acid, anthranilic acid) in the $PdCl_2(PPh_3)_2$-TsOH catalyst system increased the conversion level at the cost of selectivity to carbonylation products (Table-3, run# 7, 9). Thus, the ligands having a basic nature were effective in achieving higher carbonylation selectivity in $[PdCl_2(PPh_3)_2]$-TsOH catalyst system, whereas the ligands with an acidic nature increased the conversion of VAM with a decrease in selectivity to carbonylation products. When the acidic ligands were used along with $[PdCl_2(PPh_3)_2]$ as catalyst in the absence of TsOH, the selectivity to carbonylation products was increased at the cost of conversion over $[PdCl_2(PPh_3)_2]$-TsOH catalyst system (Table-3, run# 8^b, 10^b to 12^b).

Effect of PPh_3 concentration: The effect of phosphine ligand concentration was investigated using $[PdCl_2(PPh_3)_2]$ as catalyst (Table-4). A marginal increase in catalytic activity was observed with a small increase in PPh_3 concentration in the

TABLE-3
EFFECT OF LIGANDS IN METHOXYCARBONYLATION OF VINYL ACETATE MONOMER (VAM) USING $[PdCl_2(PPh_3)_2]$ CATALYST

No.	Ligand	Time (h)	^{a}Conversion (%)	^{a}Selectivity (%)			TOF (h^{-1})
				D	E	F	
1	–	4.5	99.89	28.06	62.18	1.87	33
2^b	–	10	99.12	43.13	45.09	10.78	28
3	Pyridine	3.5	90.01	63.35	12.91	12.77	102
4	2,2'-Bipyridine	4.5	88.23	39.35	23.24	20.38	60
5	2,2',2"-Terpyridine	4	45.28	18.09	24.33	0	10
6	1,10-Phenanthroline	4	25.01	2.61	8.19	0	1
7	Picolinic acid	2	98.97	18.01	33.35	17.55	93
8^b	Picolinic acid	4	78.41	43.94	22.25	15.57	61
9	Anthranilic acid	2.5	99.29	14.54	34.42	9.79	49
10^b	Anthranilic acid	10	99.04	45.04	25.03	19.29	34
11^b	Nicotinic acid	4	60.15	57.57	18.75	16.82	57
12^b	Acetyl acetone	4	84.09	46.96	22.77	17.88	72

Reaction conditions: $[PdCl_2(PPh_3)_2]$: 2 × 10^{-3} kmol/m^3; VAM: 1 kmol/m^3; CH_3OH: 2.4 kmol/m^3; Ligand: 4 × 10^{-2} kmol/m^3; TsOH: 8 × 10^{-3} kmol/m^3; Solvent: Toluene; Total volume: 2.5 × 10^{-5} m^3; Temperature: 373 K; P_{CO}: 5.4 MPa; Selectivity: D: Methyl-2-acetoxypropionate; E: Methyl acetate; F: Methyl lactate; ^{a}By GC analysis; ^{b}Without TsOH.

TABLE-4
EFFECT OF PPh_3 CONCENTRATION IN $PdCl_2(PPh_3)_2$ CATALYZED CARBONYLATION OF VINYL ACETATE MONOMER (VAM)

Run No.	^{b}PPh$_3$/Pd ratio	Time (h)	Conversion (%)	Selectivity (%)			TOF (h^{-1})
				A	B	C	
1	2	10	99.12	45.09	43.13	10.78	28
2	4	4.5	61.58	38.59	31.19	11.29	30
3	12	2	99.37	91.61	1.83	2.06	10

Reaction Conditions: $PdCl_2(PPh_3)_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH_3OH, 2.4 kmol/m^3; Solvent, Toluene; Total volume, 2.5 × 10^{-5} m^3; Temperature, 373 K; P_{CO}: 5.4 MPa; Selectivity: A, methyl acetate; B, methyl-2-acetoxypropionate; C, methyl lactate; PPh_3/Pd ratio was maintained by addition of required amount of PPh_3 to the reaction mixture

TABLE-5
EFFECT OF SOLVENTS IN $PdCl_2(PPh_3)_2$ CATALYZED CARBONYLATION OF VINYL ACETATE MONOMER (VAM)

Run No.	Solvent (dipole moment, debye)	[a]Conversion (%)	[a]Selectivity (%)			TOF (h^{-1})
			D	E	F	
1	Acetonitrile (3.92)	82.65	3.86	79.88	12.87	18
2[b]	Methanol (1.70)	91.56	22.27	57.69	6.70	4
3	THF (1.75)	91.42	35.67	46.42	15.08	61
4	Chlorobenzene (1.54)	97.57	34.27	54.13	9.63	70
5	Toluene (0.37)	84.09	46.96	31.41	17.88	72

Reaction conditions: $[PdCl_2(PPh_3)_2]$: 2×10^{-3} kmol/m^3; VAM: 1 kmol/m^3; CH_3OH: 2.4 kmol/m^3; acac: 4×10^{-2} kmol/m^3; Total Volume: 2.5×10^{-5} m^3; Time: 4 h; Temperature: 373 K; P_{CO}: 5.4 MPa; Selectivity: D: Methyl-2-acetoxypropionate; E: Methyl acetate; F: Methyl lactate; [a]By GC analysis; [b]Catalyst was found precipitated as Pd-black in the reaction mixture after carbonylation reaction

reaction mixture (0.2 mmol), whereas a higher concentration of PPh_3 (0.6 mmol) in the $[PdCl_2(PPh_3)_2]$ catalyst system showed very poor carbonylation activity, yielding more methyl acetate (91.61%), though maximum conversion (99.37%) could only be achieved in 2 h.

Effect of solvents: The effect of different solvents was carried out at 373 K and 5.4 MPa using $[PdCl_2(PPh_3)_2]$ as catalyst and acetyl acetone as a ligand (Table-5). The dipole moment of solvents was correlated with the catalyst activity and it was observed that non-polar solvents having less dipole moment were better solvents for VAM methoxycarbonylation reaction. As a trend, the activity was found to increase with a decrease in polarity of a solvent (dipole moment). This trend in activity was found inapplicable for methanol as solvent because substantial amount of palladium catalyst was found precipitated in the reaction mixture when the reactor was emptied, rendering it inaccessible for the carbonylation reaction (Table-5, run# 2[b]). Similarly, an increase in the dipole moment of solvent increased the selectivity to methyl acetate and decreased the selectivity to carbonylation products. The non-polar solvents probably help to stabilize the neutral catalytic Pd-H species in the reaction medium, as the reaction mechanism proceeds through Pd-H species [23]. The use of toluene as a non-polar solvent resulted in high activity (72 h^{-1} TOF) with great selectivity for carbonylation products (65%).

Hydrolysis of methyl-2-acetoxypropionate and methyl lactate to lactic acid: Methyl-2-acetoxypropionate isolated from reaction mixtures was hydrolyzed to DL-lactic acid using various acid catalysts. Hydrolysis of methyl-2-acetoxy propionate generated acetic acid in the reaction mixture (**Scheme-II**), which can act as a catalyst due to its acidity that make the hydrolysis of methyl-2-acetoxy propionate faster than that of methyl lactate (Table-6). Heterogeneous catalyst Amberlite IR-20 resin was used for hydrolysis, which gave 43% conversion in 3 h and successive recycle maintained the activity. Methyl lactate was extracted from the carbonylation reaction mixture and hydrolyzed using various acidic catalysts. TsOH was found to be the best catalyst for hydrolysis of methyl lactate. Heterogeneous acidic catalysts also showed comparable activity even in successive recycles (Table-6).

TABLE-6
HYDROLYSIS OF METHYL-2-ACETOXYPROPIONATE

Run No.	Catalyst (g or mL)	[a]Conversion (%)	Selectivity (%)	Time (h)
1	TsOH (0.191 g)	100 (65.14)	100	3
2	35% HCl (1 mL)	95.23 (58.05)	98.32	3
3	Amberlite IR 20 (0.5 g)	43.10 (38.27)	94.5	3
4	[b]Amberlite IR 20	41.77 (37.89)	96.58	3

Reaction conditions: Methyl-2-acetoxypropionate: 6.66×10^{-1} kmol/m^3; Water: 1.5×10^{-5} m^3; Temperature: 353 K; [a]Coversion in parenthesis for Methyl lactate, [b]Catalyst recycled from run no. 3

Conclusion

Methoxycarbonylation of vinyl acetate monomer (VAM) was investigated using various Pd-catalysts at 5.4 MPa CO partial pressure and 373 K. The use of quaternary ammonium halide TBAX with $PdCl_2(PPh_3)_2$ as catalyst enhanced VAM conversion and selectivities to carbonylation products (methyl-2-acetoxypropionate and methyl lactate). Basic ligands increased the catalytic activity of $PdCl_2(PPh_3)_2$ in the presence of TsOH, whereas acidic ligands increased catalyst activity in the absence of TsOH. The polarity of solvents was shown to have a substantial effect on catalytic activity. Decrease in the catalytic activity was observed with increasing the polarity of solvent. The non-polar solvents are an effective reaction medium for this reaction. Hydrolysis of methyl-2-acetoxypropionate to DL-lactic acid was carried out using acid catalysts to achieve a high yield. The methoxycarbonylation of VAM provides an economic and environmentally benign catalytic method for the synthesis of a precursor methyl-2-acetoxypropionate, which can be easily converted to lactic acid by hydrolysis.

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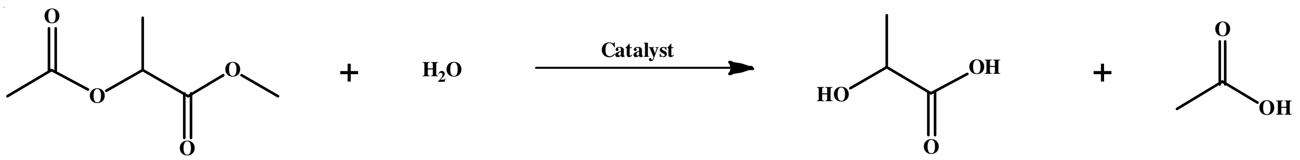

Scheme-II: Hydrolysis of methyl-2-acetoxypropionate to lactic acid

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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