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Acrylic acid oxidation to synthesize methyl 3,3-dimethoxypropionate

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Methyl 3,3-dimethoxypropionate was prepared via the oxidation of acrylic acid by oxygen in methanol over $PdCl_2/CuCl_2$ catalyst. An acrylic acid conversion of 95.2% with a methyl 3,3-dimethoxypropionate selectivity of 90.6% was obtained at 35 °C and 5 atm. The reaction pathway might be that the esterification of acrylic acid in methanol was the first step, then methyl acrylate reacted with oxygen to form an intermediate aldehyde, which could react with methanol to form methyl 3,3-dimethoxypropionate.

KEY WORDS: acrylic acid oxidation; catalyst; methyl 3,3-dimethoxypropionate.

1. Introduction

Acrylic acid is an important monomer for poly acrylate synthesis, and also due to it's multifunctional-group structure, it could be a potential intermediate for the synthesis of other fine chemicals. If the terminal carbon–carbon double bond of acrylic acid can be oxidized, it could be converted to important synthesis intermediates, such as alkyl 3,3-dialkoxypropionates and dimethyl malonate, which are extensively used in organic synthesis. Alkyl 3,3-dialkoxypropionates are used to synthesize a variety of compounds, such as coumains [1], spermine [2], loganin [3], wheat fungicide silthiofams [4,5], and 1-amino-pyrrole-3-carboxylic acid derivatives [6]. Previously, the preparation of alkyl 3,3-dialkoxypropionate was not satisfactory because the high cost of raw materials and low overall yield. In recent years, Wacker reaction and similar reactions were used to synthesize the mentioned alkyl 3,3-dialkoxypropionate. In these reactions, terminal olefins bearing electron-withdrawing groups were oxidized to the target products. Through the reaction, methyl 3,3-dimethoxypropionate was synthesized in high yield by oxidizing methyl acrylate in supercritical CO_2 [7]. However, a very high pressure (130 atm) was employed. Arata Kishi et al. investigated the catalytic oxidation of ethyl acrylate over $Pb(OAc)_2$ and NPMoV/C [8]. An ethyl 3,3-diethoxypropionate yield of 83% was obtained at 1 atm pressure within 20 h. Both ethyl acrylate and methyl acrylate are relatively expensive chemicals. It is highly desired to directly make use of acrylic acid to synthesize methyl 3,3-dimethoxypropionate. However, there was no report in acrylic acid direct oxidation. In this paper, we report the direct oxidation of acrylic acid by oxygen in methanol to synthesize methyl 3,3-dimethoxypropionate.

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2. Experimental

All of the reactions were carried out in a stainless steel microbatch reactor with an inside poly tetrafluoroethylene (PTFE) container (6.0 mL). The reactor was installed with an oxygen supplying and pressure-releasing line, which can pressurize the reactor to desired pressure with oxygen and release the pressure of the reactor after reaction. The pressure of oxygen was controlled by a pressure regulator. An aluminum heating mantle was used to heat up the reactor. Before reaction, catalyst and reactants were loaded into the reactor (with a magnetic stirring bar), then sealed the reactor and pressurized it with oxygen to 2 atm, and then turned off the oxygen supplying valve and slowly turned on the pressure releasing valve to vent the over space of the reactor. The process was repeated 4–5 times to clear the reactor, and then shut down the vent valve. Finally, the reactor was heated to the desired reaction temperature, and then was pressurized with oxygen to desired pressure to carry out reaction under stirring. After the reaction was completed, the reactor was cooled to room temperature, then turned off the oxygen supplying valve and slowly turned on the vent valve to release the pressure. Finally, the reactor was opened, and the reaction mixture was analyzed.

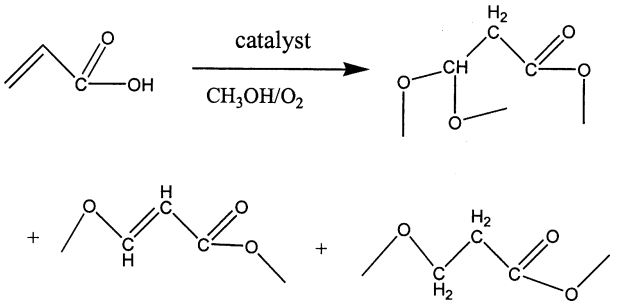
In all of the reactions, the amount of acrylic acid or methyl acrylate and methanol used in each reaction were 13 mmol and 52 mmol, respectively. If $PdCl_2$ or $RuCl_3$ was used as catalyst, the amount in each reaction was 0.056 mmol. If MCl_2 (M was Cu, Fe, Ni, or Mn.) was used as catalyst, the amount was 0.45 mmol in each reaction. The reactions were carried out at different temperature and pressure under stirring. The sample analysis was conducted on a GC (Agilent 6890N) and a GC-MS (Agilent 6890N/5973N).

3. Results and discussion

Our studies showed that pure acrylic acid or acrylic acid aqueous solution did not react with oxygen at 55 °C over $PdCl_2/CuCl_2$ catalyst. Also, when pure methyl acrylate reacted with oxygen at 55 °C over $PdCl_2/CuCl_2$ catalyst, the GC-MS analysis showed trace of acrylic acid and methyl 3,3-dimethoxypropionate. When methyl acrylate and methanol mixture (mole ratio 1:3) reacted with oxygen over $PdCl_2/CuCl_2$ catalyst, methyl 3,3-dimethoxypropionate was formed as a major product with a methyl acrylate conversion of 100% and methyl 3,3-dimethoxypropionate selectivity of 90.4% at 55 °C and 5 atm (oxygen pressure).

As listed in table 1, when acrylic acid reacted with oxygen in methanol over catalysts, methyl 3,3-dimethoxypropionate was formed as major product, while methyl 3-methoxypropionate and methyl 3-methoxyacrylate were formed as by-products in some of our reactions. The reaction is shown in scheme 1. These results indicate that, for the oxidation of acrylic acid or methyl acrylate, methanol is an important reactant and solvent. In all the reactions, 3,3-dimethoxypropionic acid was not detected. Hence, acrylic acid cannot be directly oxidized by oxygen before esterification.

Other metal chlorides or the combinations of $PdCl_2$ with other metal chlorides were also tested as catalysts for acrylic acid oxidation in methanol. The results are listed in table 1. It can be found that $RuCl_3$ showed very low activity for acrylic acid oxidation. $PdCl_2$ showed high activity and high methyl 3,3-dimethoxypropionate selectivity. The only by product was methyl 3-methyloxylacrylate (scheme 1). The combination of $PdCl_2$ with



Scheme 1

$CuCl_2$ was the most efficient catalyst. 95% of acrylic acid conversion with 90.6% of methyl 3,3-dimethoxypropionate selectivity was obtained at 35 °C over $PdCl_2/CuCl_2$ catalyst. The other combinations, such as $PdCl_2/NiCl_2$, $PdCl_2/MnCl_2$, and $PdCl_2/FeCl_2$ did not show higher activities than $PdCl_2$ catalyst.

In table 1 from entries 7 to 8, with the increase of reaction temperature from 35 °C to 55 °C, acrylic acid conversion increased and reached a maximum conversion of almost 100% at 55 °C. However, when the reaction temperature increased from 65 °C to 95 °C, the conversion decreased (entries 9–11). The possible reason might be that, since there was water formed in the oxidation reaction, possibly, the higher reaction temperature shifted the esterification reaction equilibrium of acrylic acid towards the hydrolysis direction of methyl acrylate. At this case, there was a part of acrylic acid could not be esterified (Previously, we showed that oxygen can not directly oxidize acrylic acid.). Hence, the acrylic acid conversion decreased at high reaction temperature. At the same time, the total selectivity of the by

Table 1
Catalyst performance for acrylic acid oxidation in methanol

Entry	Catalyst	t (h)	T (°C)	P (atm)	X (%)	Selectivity			TON
						S_1	S_2	S_3	
1	No	6	55	5	0	0	0	0	0
2	$RuCl_3$	6	55	5	0.8	100	0	0	1.9
3	$PdCl_2$	6	55	5	42.6	95.2	4.8	0	99.9
4	$PdCl_2/NiCl_2$	6	55	5	30.5	90.4	9.6	0	70.9
5	$PdCl_2/FeCl_2$	6	55	5	27.0	93.1	6.9	0	62.7
6	$PdCl_2/MnCl_2$	6	55	5	25.2	92.6	5.6	1.8	58.5
7	$PdCl_2/CuCl_2$	6	35	5	95.2	90.6	9.4	0	221.0
8	$PdCl_2/CuCl_2$	6	55	5	100	77.3	21.9	0.7	232.1
9	$PdCl_2/CuCl_2$	6	65	5	100	82.7	16.2	1.0	232.1
10	$PdCl_2/CuCl_2$	6	75	5	64.9	81.2	13.5	5.2	150.6
11	$PdCl_2/CuCl_2$	6	95	5	20.4	53.2	0	46.8	47.4
12	$PdCl_2/CuCl_2$	6	55	7.5	100	71.6	28.4	0	232.1
13	$PdCl_2/CuCl_2$	6	55	10	100	72.4	27.6	0	232.1
14	$PdCl_2/CuCl_2$	6	55	12.5	100	79.9	20.1	0	232.1
15	$PdCl_2/CuCl_2$	0.17	55	5	7.9	100	0	0	18.4
16	$PdCl_2/CuCl_2$	1	55	5	49.1	82.3	16.5	1.2	114.0

Note: t, reaction time; T, reaction temperature; P, oxygen pressure; X, acrylic acid conversion; S_1, the selectivity of methyl 3,3-dimethoxypropionate; S_2, the selectivity of methyl 3-methoxyacrylate; S_3, the selectivity of methyl 3-methoxypropionate; TON, turnover number (calculated as mole acrylic acid to per mole of catalyst).

products methyl 3-methyloxyacrylate and methyl 3-methoxypropionate increased.

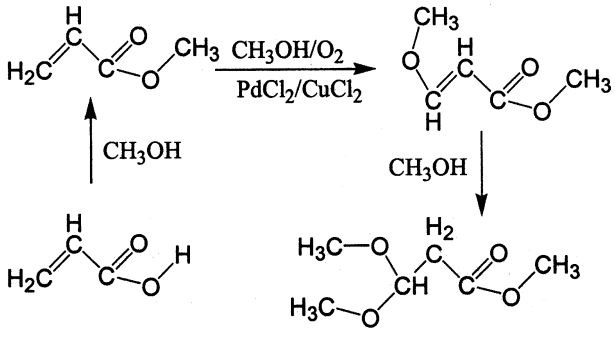
Oxygen pressure also affected the acrylic acid oxidation. When oxygen pressure increased from 5 to 7.5 atm, the selectivity of methyl 3,3-dimethoxypropionate decreased (table 1, entries 8 and 12) and when oxygen pressure increased from 7.5 to 12.5 atm, the selectivity of methyl 3,3-dimethoxypropionate increased (table 1, entries 12–14). However, the selectivity did not show obvious improvement comparing with that at 5 atm. Based on the results, the optimum oxygen pressure for acrylic acid oxidation was found to be 5 atm.

One of the by products, methyl 3-methoxypropionate seems to be a direct addition product of methanol to methyl acrylate. In order to prove the prediction, we carried out reaction between methyl acrylate and methanol without oxygen at 85 °C over $PdCl_2/CuCl_2$ catalyst. Methyl acrylate (20.0% conversion) was converted to methyl 3-methoxypropionate (79.4% selectivity, not listed in table 1) in the reaction. At the reaction conditions, methyl 3-methoxypropionate might be oxidized to methyl 3,3-dimethoxypropionate. In order to explore the possibility of this reaction, we carried out the reaction between methyl 3-methoxypropionate and oxygen over $PdCl_2/CuCl_2$ catalyst. In the experiments, 0.80 mL of methyl 3-methoxypropionate, 2.20 mL of methanol, 10.0 mg of $PdCl_2$, 60.0 mg of $CuCl_2$ were loaded in to the high-pressure batch reactor to carry out reaction at 120 °C and 5.0 atm of oxygen pressure. After 5 h of reaction, only trace of 3-methoxypropionic acid was detected. 3-methoxypropionic acid might come from the hydrolysis reaction of methyl 3-methoxypropionate. The result proved that methyl 3-methoxypropionate cannot be oxidized to methyl 3,3-dimethoxypropionate at our reaction conditions. Hence, methyl 3-methoxypropionate was not a reaction intermediate for methyl 3,3-dimethoxypropionate formation.

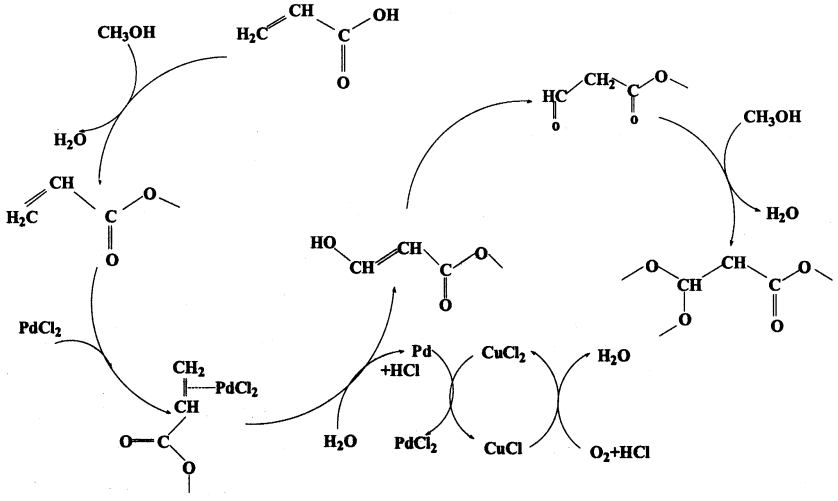
Based on the results, the acrylic acid oxidation might follow the following two possible reaction pathways schemes 2 and 3.

According to scheme 2, acrylic acid is esterified to methyl acrylate and then the methyl acrylate combined with $PdCl_2$ to form an intermediate. In the following reaction, water attacks the intermediate to form a hydroxyl group on the terminal carbon atom, which could isomerize to aldehyde, then aldehyde reacts with methanol to form methyl 3,3-dimethoxypropionate. At the same time, $PdCl_2$ was reduced to Pd, and then Pd was oxidized to $PdCl_2$ by $CuCl_2$, while $CuCl_2$ was reduced to CuCl. Finally, CuCl was oxidized to $CuCl_2$ by O_2 to complete the catalytic cycle.

When methyl acrylate with $PdCl_2$ and $CuCl_2$ was loaded into reactor, without oxygen, the results showed that only trace of acrylic acid and methyl 3,3-dimethoxypropionate was formed. Hence, the methoxyl group of methyl 3,3-dimethoxypropionate might come from methanol, which might come from the hydrolysis of methyl acrylate. The results indicated that methanol was necessary for methyl acrylate oxidation. The reason that methyl acrylate could be easily oxidized in methanol might be that the methyl 3,3-dimethoxypropionate formation reaction from metha-



Scheme 3



Scheme 2

nol and intermediate aldehyde (shown in scheme 2) accelerated the methyl acrylate oxidation reaction, therefore accelerated the acrylic acid esterification reaction. Our results support the assumption in scheme 2.

Another possible reaction pathway is shown in scheme 3, the first step is the esterification of acrylic acid with methanol. The second step is the co-oxidation of methyl acrylate with methanol by oxygen to form methyl 3-methoxyacrylate. The subsequent reaction might be an addition reaction of methanol on the carbon–carbon double bond of methyl 3-methoxyacrylate. Our results proved that at suitable oxygen pressure (about 7.5–10 atm), methyl 3-methoxyacrylate could be formed with high selectivity (table 1, entries 12 and 13). However, if methyl 3-methoxyacrylate was formed as a primary product and methyl 3,3-dimethoxypropionate was formed from the methanol addition reaction on methyl 3-methoxyacrylate, at the beginning of the reaction, we should obtain higher selectivity of methyl 3-methoxyacrylate. However, the data in table 1 (entry 15) showed that within the primary 10 min of the reaction, we did not detect methyl 3-dimethoxyacrylate as product. Hence, methyl 3-methoxyacrylate was not a reaction intermediate for methyl 3,3-dimethoxypropionate formulation. Hence, our experiment results do not support the assumption of scheme 3.

4. Conclusion

Our investigation indicates that acrylic acid can be highly efficiently oxidized to methyl 3,3-dimethoxypropionate in methanol by using $PdCl_2/CuCl_2$ as catalyst. An acrylic acid conversion of 95.2% with a methyl 3,3-dimethoxypropionate selectivity of 90.6% was obtained at 35 °C within 6 h reaction. In the reaction, methanol acted as both reactant and solvent. The reaction mechanism is possibly that acrylic acid reacted with methanol to form methyl acrylate, then methyl acrylate might react with oxygen over $PdCl_2/CuCl_2$ catalyst to form intermediate aldehyde. Finally, the aldehyde reacted with methanol to form methyl 3,3-dimethoxypropionate. The methyl 3,3-dimethoxypropionate formation reaction from the intermediate aldehyde and methanol might accelerated the methyl acrylate oxidation reaction, as a result also shifted the acrylic acid esterification reaction towards the methyl acrylate formation. This reaction mechanism finally led to all of the acrylic acid esterification and oxidation to form methyl 3,3-dimethoxypropionate in methanol.

Acknowledgments

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