

One-step synthesis of ester from alkene

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Abstract

A one-step synthesis of ethylacetate from a feed mixture of ethene, oxygen, and water using a supported Pd and silicotungstic acid catalyst was demonstrated. At about 180 °C and 25% ethene conversion, ethylacetate could be produced with 46% selectivity, with 34% acetic acid and ethanol that could be recycled. The catalyst was believed to be bifunctional, with Pd providing the oxidation function and the silicotungstic acid providing the acidic function. And this catalyst system had an activity that could produce isopropylacrylate from a feed mixture of propene, oxygen, and water.

1 Introduction

Carboxylic acid esters are used in a wide range of applications. They are used, for example, as plasticizers, solvents, surface-active agents, and flavor and perfume materials. There are many known methods to produce esters. The most common method is the esterification, which is a reaction of alcohol with carboxylic acid^{1,2}. For example, ethyl acrylate is synthesized from ethyl alcohol and acrylic acid, and ethyl acetate from ethyl alcohol and acetic acid. An acidic catalyst, which can be a mineral acid, or polymeric material containing chemically-bound acid groups, such as sulfonated polystyrene, is commonly used in the esterification. Other methods are also available such as acylation with acryl halides, carboxylic anhydrides or ketenes, carbonylation of alkenes in an alcoholic solution, alcoholysis of nitriles, and acylation of alkenes with carboxylic acid^{1,2}. The synthesis of ethyl acetate by gas phase reaction of ethene and acetic acid over a solid acid catalyst was reported, such as supported heteropoly acid and Amberlyst³.

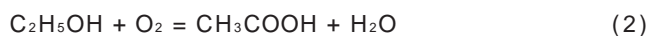
It is interesting to note that a Pd-M-H₃PO₄/SiO₂ catalyst (M=V, Mo, W, and Cr) was reported not to produce any ethyl acetate but only acetaldehyde at 150 °C, using a feed containing C₂H₄/O₂/H₂O/N₂=50/7/30/13⁴. The oxidation of ethene to acetic acid using a heteropolyacid-Pd/SiO₂ catalyst was also reported⁵.

We have recently studied a one-step synthesis of ethyl acetate by reaction of ethene, water and oxygen over a catalyst. Here we report the results of this study. A conceptual scheme of the one-step synthesis can be accomplished is as follows:

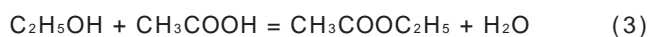
A catalyst induces the hydration of ethene to ethanol



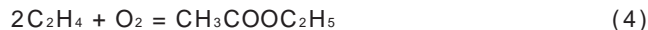
Some of ethanol is then selectively oxidized to acetic acid.



Finally, ethyl acetate is produced by the esterification of ethanol with acetic acid over a catalyst.



Thus the overall reaction is



Such a one-step process has the advantage of starting with reactants, which are much less expensive than corresponding alcohols and acids, or anhydrides, halides, and nitriles. If the reactions occur selectively, the produced mixture coming out of a reactor consists of desired products and recyclable intermediates.

According to the conceptual reaction scheme described in this paper, in order for this one-step synthesis to be successful, a multi-functional catalyst is required. The catalyst needs to contain a selective oxidation function for the oxidation of ethanol to acetic acid, and an acid function for hydration and esterification. Ideally, the reaction condition would be such that all three reactions occur simultaneously at about the same rate. For example, high temperature might be unfavorable because the equilibrium constant of ethene to ethanol in the hydration reaction decreases as temperature rises. In these experiments, the acid function was provided by a heteropolyacid, and the oxidation function was provided by palladium. Such a bifunctional-bicomponent system is advantageous over a single component system (e.g. heteropolyacid) that requires separate reaction conditions to activate each function⁶.

2 Experimental

The catalysts were prepared using a silica support (Davison 62,

60/80mesh, 250m²/g) which had been washed with 1 M nitric acid at 80 °C and deionized water to remove mineral impurities, and then dried and calcined at 520 °C for 6h. Pd was introduced into silica as Pd chloride (Aldrich) dissolved in 1 M HCl using the incipient wetness technique. The impregnated samples were calcined in a flow of O₂ in He (2/8 molar ratio) at 350 °C for 2h and then in H₂ at 300 °C for 3h. Silicotungstic acid (H₄SiW₁₂O₄₀, Nippon Inorganic Color and Chemical Co., Ltd.) was impregnated onto the Pd/SiO₂ samples by incipient wetness using its aqueous solution, and dried in air at 110 °C overnight. All the catalysts were treated at 180 °C in helium stream (or atomosphere) for 1h before reaction. Reactions were conducted in a 6.3mm i.d. stainless tubular reactor. The reactor pressure was between 200 to 330 kPa, and 5ml of catalyst was used. The reactor was heated by an electrical furnace equipped with temperature controllers. The flow rates of ethene, oxygen and helium were controlled by mass flow controllers. Liquid water was introduced by a syringe pump and then vaporized in a heated zone. Typically, the gas flow rates at atmospheric pressure and room temperature were 10(ethene), 2.5(O₂), 2.0(He), and 6.0(H₂O)

ml/min. Reaction products were analyzed by on-line gas chromatography using a Parapak Q column. Typically, the reaction was carried out for 4 to 6 h.

3 Results and Discussion

Table 1 shows the results using catalysts of different Pd and H₄SiW₁₂O₄₀(SiW) contents. Each datum represents an average of at least three separate product analyses.

Under similar conditions, a 5wt.% Pd/SiO₂ catalyst produced acetic acid with only 0.5% yield and 2.5% CO₂, whereas a 44 wt.% SiW/SiO₂ sample produced <2% yield acetic acid, 2.5% ethanol, and <1% acetaldehyde. No ethyl acetate was obtained from the above two catalysts. The low yield of acetic acid from the Pd/SiO₂ catalyst makes it unlikely that the function of Pd is to oxidize ethylene to acetic acid(Eq.(5)), which then reacts with ethene over SiW to form ethyl acetate. This low yield cannot account for the yields of ethyl acetate over the SiW/Pd-SiO₂ catalysts.



Table 1
Ethene conversions, yields, and selectivities of various products over several SiW/1.5wt.% Pd-SiO₂ catalysts^a

Catalyst		C ₂ conversion (%)	Yield (Selectivity) ^b (%)				
Pd (wt%)	SiW/Pd (wt. Ratio)		Ethyl acetate	Acetic acid	Ethanol	Acetaldehyde	CO ₂
1.5	40/1.5	2.0	0.0 (0)	0.0 (0)	1.7 (85)	0.3 (15)	0.0 (0)
1.5	60/1.5	16.4	6.5 (40)	4.2 (26)	2.2 (13)	0.6 (4)	2.9 (18)
1.5	80/1.5	24.4	11.2 (46)	6.1 (25)	2.1 (9)	0.9 (9)	4.1 (17)
1.5	200/1.5	12.7	4.8 (38)	4.4 (35)	0.2 (2)	0.9 (2)	2.4 (19)
5	80/5	19.8	9 (43)	6 (29)	1.7 (8)	0.3 (14)	4 (19)
5	100/5	25.3	9.5 (38)	9.7 (38)	1.6 (6)	0.4 (2)	4 (16)

^aFeed=C₂H₄/O₂/He/H₂O=10/2.5/2/≤6ml/min; T=180–185°C, P=200–300kPa

^bCarbon-based yield and selectivity

^cSiW=H₄SiW₁₂O₄₀

Table 2
SiW/Pd-SiO₂ catalyst^a activity for ethene conversions, yields, and selectivities of various products on several reaction temperature conditions^b

Reaction temperature	C ₂ conversion (%)	Yield (Selectivity) (%)				
		Ethyl acetate	Acetic acid	Ethanol	Acetaldehyde	CO ₂
140°C	10.7	2.7 (29)	4.1 (44)	0.4 (4)	0.4 (4)	1.7 (18)
160°C	18.9	9.7 (47)	6.1 (30)	1.1 (5)	0.4 (2)	3.4 (16)
170°C	23.7	11.2 (46)	7.1 (29)	1.4 (6)	0.3 (1)	4.2 (17)
180°C	25.6	11.5 (44)	7.5 (29)	1.5 (6)	0.4 (2)	5.0 (19)

^aH₄SiW₁₂O₄₀/1.5wt.%Pd-SiO₂=80/100

^bFeed=C₂H₄/O₂/He/H₂O=10/2.5/2/≤6ml/min; P=200–300kPa

Table 3
SiW/Pd-SiO₂ catalyst^a activity for ethene conversions, yields, and selectivities of various products on several reaction pressure conditions^b

Reaction pressure	C ₂ conversion (%)	Yield (Selectivity) (%)				
		Ethyl acetate	Acetic acid	Ethanol	Acetaldehyde	CO ₂
200kPa	16.0	4.8 (43)	4.4 (39)	1.7 (15)	0.3 (3)	0.0 (0)
230kPa	17.5	6.5 (37)	5.2 (30)	2.2 (13)	0.6 (3)	2.9 (17)
260kPa	17.2	8.1 (39)	5.4 (26)	2.1 (10)	0.9 (4)	4.1 (20)
330kPa	19.8	10.0 (51)	6.0 (31)	0.2 (1)	0.9 (5)	2.4 (12)

^aH₄SiW₁₂O₄₀/1.5wt.%Pd-SiO₂=80/100

^bFeed=C₂H₄/O₂/He/H₂O=10/2.5/2/≤6ml/min; T=180–185°C

Better activity of SiW/Pd-SiO₂ at higher reaction temperature is shown in table 2. Although optimal reaction temperature of hydration of ethene was around 150 °C over heteropolyacid catalysts⁴⁾, yield of acetic acid was obviously increased at temperatures over 170 °C. These data indicate that oxidation activity of SiW/Pd-SiO₂ is enhanced at the temperature.

As shown in Table 3, evidently, acetic acid was produced more at higher reaction pressure. Higher reaction pressure was advantageous for desired element reactions, hydration and oxidation of ethene, stoichiometrically (Eq.(4)).

The data show that, under these conditions, ethyl acetate could be produced with almost 50% selectivity. Very importantly, the total selectivity for the desired product and the intermediates that can be recycled (ethanol and acetic acid) was as high as 80%. Carbon (20%) was wasted mostly as CO₂.

An optimal Pd/SiW ratio appears to be about 1/15 to 1/60 for high yields of ethyl acetate. Since the overall yield comes from the combination of Eq.(1) to Eq.(3), both catalytic functions (Pd and SiW) are required. Small Pd/SiW ratio is probably a result of higher dispersion of Pd on SiO₂ and its higher catalytic activity per unit surface area.

Other supports were also tested, including alumina and activated carbon. For example, with a carbon-supported catalyst that contained SiW, Pd, and carbon in a weight ratio of 0.8, 0.05 and 1, an ethene conversion of 25% was obtained, with selectivity for ethyl acetate, acetic acid, and ethanol of 36, 35, and 7%, respectively.

Thus, we have demonstrated that it is possible to synthesize ethyl acetate from rather inexpensive reactants in a one-step, catalytic process reaction. The reaction yields only a small amount of unwanted byproducts. It is quite possible that with further optimization of catalyst composition and reaction conditions, such as temperature, feed composition, and pressure, can increase the yield and selectivity for ethyl acetate.

In addition to ethyl acetate, other esters can be produced from

appropriate alkenes. For example, when a mixture of C₃H₆, O₂, H₂O, and He, in a volume ratio of 10/5.5/1.6/1, was passed over a catalyst bed at 120 °C containing H₃PW₁₂O₄₀, Pd and SiO₂, at a total pressure of 500kPa, 37% conversion of propene was obtained. The carbon selectivity of various products were isopropylacrylate 36% (11.9% yield), acrylic acid 13% (4.2% yield), 2-propanol 11% (3.7% yield), isopropylacetate 7% (2.2% yield), acetone 26% (8.8% yield), and diisopropylether 7% (2.3% yield).

4 Conclusion

A one-step synthesis of ethyl acetate from a feed mixture of ethene, oxygen, and water using a supported Pd and silicotungstic acid catalyst was reported. At about 180 °C, 25% ethene conversion was obtained and ethyl acetate could be produced with as high as 46% selectivity, together with 34% acetic acid and ethanol that could be recycled. The catalyst was believed to be bifunctional, with Pd providing oxydation function and silicotungstic acid providing acidic function.

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アルケンを原料としたエステル的一段合成

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Pdとシリコタングステン酸を担持したシリカを触媒として、エチレン、酸素、水を原料とした酢酸エチルの一段合成を試みた。この触媒は、Pdの酸化活性とシリコタングステン酸の強酸性との複合活性により、それぞれエチレンの酸化及び水和、そしてエステル化反応に必要な機能を併せ持っている。反応温度180 °Cでエチレンの転換率が25%となり、その時の酢酸エチルの選択率は46%以上であった。同時に酢酸とエタノールが合わせて34%の選択率で得られ、これらをリサイクルすれば、更なる高収率が期待される。また、プロピレン、酸素、水を原料とした反応から、アクリル酸イソプロピルの生成が確認された。