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Low Pressure Ethenolysis of Renewable Methyl Oleate in a Microchemical System

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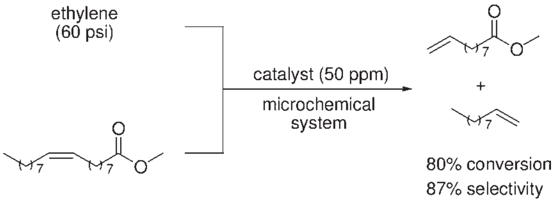
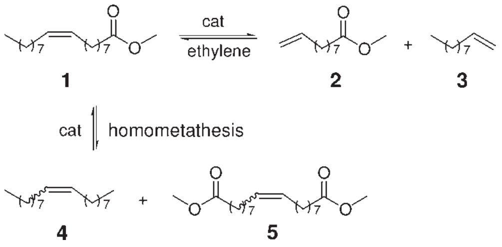
ABSTRACT



A microchemical system for ethenolysis of renewable methyl oleate was developed, in which the dual-phase, microfluidic design enabled efficient diffusion of ethylene gas into liquid methyl oleate through an increased contact area. The increased mass transfer of ethylene favored the formation of desired commodity chemicals with significantly suppressed homometathesis when compared to the bulk system. In addition to higher selectivity and conversion, this system also provides the typical advantages of a microchemical system, including the possibility of convenient scale-up.

The generation of useful, low molecular weight chemicals from renewable natural resources is an important research topic throughout the fields of chemistry and chemical engineering. Because of environmental challenges and potential economic advantages, the search for new feedstock sources and the development of chemical and biological processes to utilize the new feedstocks are the focus of much research.[1] Ruthenium catalysts, which have become useful for organic synthesis and polymer chemistry, have been tested in the olefin methathesis of internal olefins with ethylene, known as ethenolysis, which can be used to produce the desired low molecular weight products from renewable seed oils (eq 1).[2]

Early studies of the ethenolysis of natural seed oils showed promise but was limited by the high sensitivity of the traditional molybdenum, tungsten, and rhenium catalysts. The advent of ruthenium catalysts with low sensitivity but high activity has spurred a renewed interest in ethenolysis, but limited selectivity and conversion have hampered progress to commercially viable processes. Homometathesis continues to be a troubling competing reaction which reduces the yield.



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Microchemical systems have provided new strategies and new challenges as new process techniques.[3] The benefits of precise control of reaction variables and high surface area-to-volume ratios are manifest in reduced

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waste, higher yield, and reduced reaction times. Furthermore, the difficulties of scale-up can largely be avoided by simple parallelization of small-scale microfluidic test reactors. In addition to traditional, one-step microchemical reactions, several consecutive reactions, including separation, purification, and detection, have been successfully integrated as complete microchemical processes.[4]

A particularly challenging type of microchemical system is the heterogeneous reaction involving any combination of the gas, liquid, and solid phases.[5] The heterogeneous reactions between gas and liquid are mainly conducted with two main modes of contact:[6] one with the two phases flowing in contact in parallel, the other with alternative bands of gas bubbles and liquid slugs. In a recent report we described a microchemical system with the former mode of contact mediated by a PDMS (polydimethylsiloxane) membane.[7] As an alternative to this strategy, however, we feel the segmented mode of contact has its own unique advantages due mainly to the simple, convenient setup and a broader choice of available capillary materials, allowing better chemical stability and mechanical strength even at high pressure. Herein, we report a facile and efficient microchemical ethenolysis under various reaction conditions, through the continuous segmented flow of ethylene and methyl oleate in a capillary tube with a 0.5 mm inner diameter. Moreover, the reaction was performed nearly solvent-free, except for a minimun amount of toluene to dissolve the catalyst (1.0 mg of catalyst in 2.0 mL of toluene), which avoids the use of excess organic solvent to facilitate the dissolution of ethylene gas as has been reported.[8] The poor solubilty of ethylene in methyl oleate (mole fraction of ethylene/methyl oleate = 0.108, 60 psi)[2a] and the slow diffusion of ethylene into the solution favor homometathesis instead of the desirable ethenolysis. Overcoming the bias for homometathesis suggests two straightfoward strategies: developing catalysts with a high kinetic selectivity for ethenolysis, or engineering processes to drive ethylene into the reaction. The engineering approach was the main strategy of this work and was accomplished by increasing the contact area between methyl oleate and ethylene, thereby maximizing the transfer of the ethylene into the methyl oleate phase with high diffusion efficiency.[6]

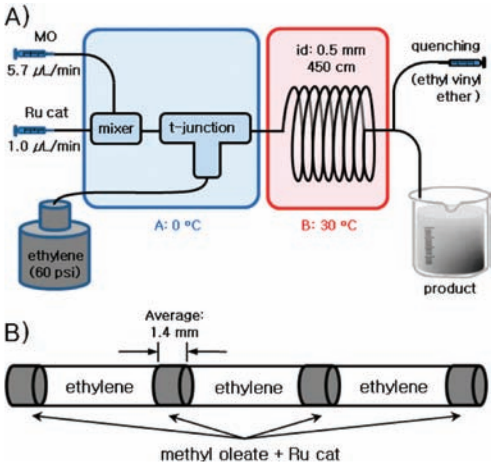

Figure 1. (A) Microchemical ethenolysis of methyl oleate (MO) with Ru catalyst (1.0 mg/2 mL toluene). (B) Segmented flow of ethylene and methyl oleate in a capillary microreactor.

In the initial design a mode of merging phases which is a general approach for reactions of this type was adopted (see Supporting Information for the system, Figure 1SA). Ethylene gas and methyl oleate were mixed in the first T-junction where slugs of liquid formed in the gas flow. In the second T-junction the flow was merged with the catalyst solution to form larger liquid slugs in the gas flow. However, this system resulted in an irregular distribution of catalyst in the methyl oleate due to slight variations in the flow rate between the two T-junctions. Because of the unsatisfactory results, the mixing order was changed so that the catalyst (at 1.0 μL/min) and substrate (at 5.7 μL/min) were mixed first and the ethylene gas was added second (Figure 1). This created the potential for a deleterious side reaction when the catalyst and substrate were mixed with no ethylene, but this was mitigated by lowering the temperature in the section between the T-junctions. The lower temperature also was expected to facilitate the diffusion of ethylene into solution. The cooled mixture of catalyst and methyl oleate was quickly saturated with ethylene injected in the second T-juction and then heated to start the reaction, taking advantage of the rapid heat transfer of microchemical systems.[3] The flow rate of the solution, and consequently the retention time, was finely controlled by a peristaltic pump instead of the more general approach of regulating the back pressurre.

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A noticeable shortening of the length of ethylene bubbles was observed through the length of the microreactor, a not unexpected observation as ethylene is consumed during the reaction.[9] The pressure drop across the length of the microreactor caused by the increased friction of the segmented liquid flow was worrisome because of the pontentially variable solubility of ethylene, but the pressure at the exit was measured to be 56 psi when the inlet pressure was set to 60 psi. The pressure differential and corresponding solubility difference were thus concluded to be negligible.

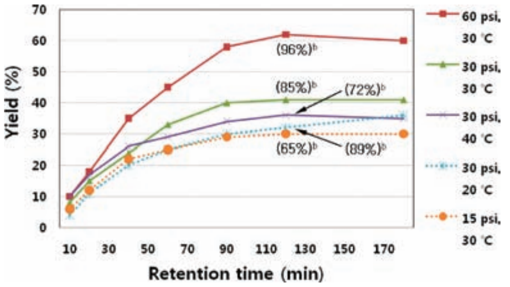

Figure 2. Ethenolysis under different temperature and pressure conditions. Catalyst **6** (300 ppm) was used. (a) Yield (%) = conversion × selectivity = (1 − final moles of **1**/initial moles of **1**) × {(**2** + **3**)/(**2** + **3** + **4** + **5**)} × 100. Conversion and selectivity were determined by GC analysis. (b) Selectivity after 120 min retention time.

As the effects of pressure and temperature in the batch system were well documented in previous reports,[2] the same variables were carefully studied in the microchemical system. With 300 ppm of catalyst **6**, the pressure was varied from 15 to 60 psi and the temperature was varied from 20 to 40 °C. The results illustrate that the pressure of ethylene has a direct impact on the yield (Figure 2).[10] Elevating the temperature over 30 °C resulted in a 5% loss in the net yield after 120 min, due to the decreased selectivity (30 psi and 30 °C: 48% conversion, 85% selectivity, 30 psi and 40 °C: 50% conversion, 72% selectivity). These good results at low temperature and high pressure are well consistent with the batch studies, where the same factors increase the selectivity and yield of ethenolysis.[2]

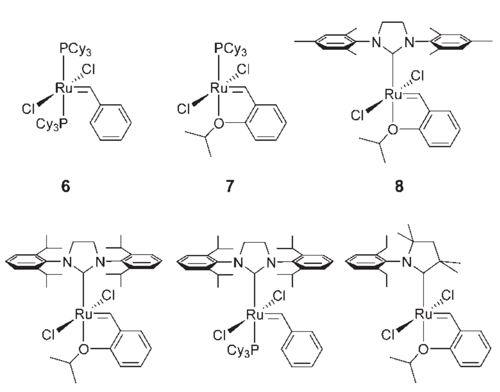

Figure 3. Ruthenium catalysts for ethenolyis of methyl oleate.

For the ethenolyis of methyl oleate **1**, six ruthenium catalysts were selected: first generation catalysts **6** and **7**; second generation catalysts **8**, **9**, and **10**; and cyclic alkylamino carbene (CAAC)-based catalyst **11**[11] (Figure 3). Each catalyst was screened at a variety of catalyst loadings, and the results were tabulated (Table 1). When catalyst **6** was used at 0 °C only a negligible amount of product was formed, confirming that no olefin metathesis occurs in the first cooled mixing zone as was expected in the redesigned system (entry 1). When the first mixing section was not cooled, an increase in homometathesis was observed as expected (entry 3). Hoveyda-type catalyst **7** was slightly more effective than catalyst **6** (entries 4 and 5), and the typical second generation catalyst **8** gave the poorest results in selectivity and yield, although the more active catalyst required less time than catalysts **6** and **7** to achieve a similar conversion (entries 6−8). The second generation catalysts **9** and **10**, which contain a sterically hindered NHC ligand, also gave lower yields than PCy_3-based catalysts **6** and **7** (entries 9−12), even though it is known that catalysts with NHC ligands have better stability and activity toward olefin metathesis than catalysts with PCy_3 ligands. In this case the homocoupling reaction, while not significant for phosphine-based catalysts **6** and **7**, accounted for about half the activity of the NHC-based

Table 1. Ethenolyses of Methyl Oleate **1** in the Microchemical System[a]

	cat. (ppm)	t (°C)	time (min)	conv (%)[c]	select (%)[d]	yield (%)[e]	TON[f]
1	**6** (150)	0	180	3	99	3.0	600
2	**6** (300)	30	120	65	96	62.4	5800
3	**6**[b](300)	30	120	66	91	60.1	5600
4	**7** (100)	30	120	39	94.8	37.0	7500
5	**7** (300)	30	120	69	93.7	64.7	4400
6	**8** (50)	40	60	58	45	26.1	11 000
7	**8** (100)	30	120	59	43.5	25.7	5400
8	**8** (100)	40	60	61	41	25.0	5300
9	**9** (50)	40	60	54	52	28.1	13 500
10	**9** (100)	40	60	57	50	28.5	6800
11	**10** (50)	40	40	61	58	35.4	22 300
12	**10** (100)	40	40	63	55	34.7	10 900
13	**11** (50)	40	60	80	87	69.6	27 200
14	**11** (100)	40	60	81	84	68.0	13 300
15	**11** (100)	40	30	72	88	63.4	12 400

[a] General reaction conditions: 60 psi ethylene, the microchemical system described in Figure 1A. Conversion and selectivity were determined by GC analysis. [b] No cooling of the mixing zone. [c] Conversion = (1 − final moles of **1**/initial moles of **1**) × 100. [d] Selectivity (%) = (**2** + **3**)/(**2** + **3** + **4** + **5**) × 100. [e] Yield (%) = conversion × selectivity/100. [f] TON = yield × [(initial moles of **1**)/(moles of cat.)].

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(9) In additon to the higher surface area-to-volume ratio, the microfluidic system is free from pressure drop, even though much of the gas is consumed, which is a property not found in batch systems.

(10) Conversion and selectivity for each condition are in the Supporting Information, Table 1S.

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catalysts **8**, **9**, and **10**. The result from catalyst **11** is the most noteworthy as the catalyst is currently the most selective catalyst known for ethenolysis among the NHC-based catalysts. Catalyst **11** gives the highest yield in this study, even when compared with phosphine-based catalysts **6** and **7**. Catalyst **11** gave a 69.6% yield with only 50 ppm catalyst and a 60 min retention time (entry 13). The selectivity is comparable to the result of the batch reaction tested at higher pressure (selectivities up to 83% were measured at 150 psi), but because of the higher conversion the yield was higher in the microchemical system.[2b] Additionally, the selectivities of catalysts **6**, **7**, **8**, **9**, and **10** are superior in the microchemical system at 60 psi compared to the batch reaction at 150 psi.

In conclusion, a microchemical system for gas–liquid dual-phase reactions was developed which was applied to the ethenolysis of methyl oleate. The results at 60 psi of ethylene were comparable to the results of batch reactions at 150 psi of ethylene. This is expected to be due to the high surface area-to-volume ratio suitable for fast mass transfer of the gas into the solution phase. The sterically hindered CAAC-based ruthenium catalyst **11** gave 80% conversion and 87% selectivity with only 50 ppm catalyst.

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Supporting Information Available. Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.