SYNTHESIS OF ACRYLATES AND METHACRYLATES FROM COAL-DERIVED SYNGAS

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BACKGROUND

Acrylates and methacrylates are among the most widely used chemical intermediates in the world. One of the key chemicals of this type is methyl methacrylate. Of the 4 billion pounds produced each year, roughly 85% is made using the acetone-cyanohydrin process, which requires handling of large quantities of hydrogen cyanide and produces ammonium sulfate wastes that pose an environmental disposal challenge. There is a clear need to develop a process that is both environmentally benign and cost-competitive. In addition, the use of coal-derived syngas to synthesize this high-value chemical allows this abundant domestic resource to be utilized more productively.

The U.S. Department of Energy and Eastman Chemical Company are sharing the cost of research to develop an alternative process for the synthesis of methyl methacrylate from syngas. Research Triangle Institute is focusing on the synthesis and testing of active catalysts for the condensation reactions, and Bechtel is analyzing the costs to determine the competitiveness of several process alternatives. The overall process to generate methyl methacrylate consists of three steps: (1) dehydrogenation *or* partial oxidation of methanol to produce formaldehyde:

$$CH_3OH \quad <==> \quad HCHO + H_2 \qquad (1a)$$
$$CH_3OH + \tfrac{1}{2} O_2 \quad <==> \quad HCHO + H_2O \qquad (1b)$$

(2) condensation of formaldehyde with a propionate (which, in turn, is derived from C_2's) to produce methacrylic acid, and (3) esterification of methacrylic acid with methanol to produce methyl methacrylate. The third step, esterification, is well-established and does not pose a challenge for process demonstration and development. The focus of this project is on the first two steps.

The keys to a successful process are (a) a catalyst for the synthesis of the propionate from C_2-feedstocks (such as ethylene), and (b) balancing the production of formaldehyde (from methanol) with the condensation reaction. Step (b) is to be carried out in a slurry reactor into which methanol, oxygen (for reaction (1b)), and the propionate are introduced. The methyl methacrylate product is drawn off as a vapor. The advantages of slurry reactor include a nearly isothermal operation and flexibility of catalyst type. Commercially, a bubble column slurry reactor would be used, allowing a significantly higher catalyst-slurry loading, and minimizing power consumption and moving agitator parts.

Results thus far show that the catalysts for the condensation of formaldehyde and the propionate are key to selectively producing the desired product, methacrylic acid, with a high yield. These condensation catalysts have both acid and base functions and the strength and distribution of these acid-base sites controls the product selectivity and yield. We are developing a predictive relationship between the acid-base nature of the catalysts and the yield of methacrylic acid/methyl methacrylate.

OVERALL CHEMISTRY FOR METHYL METHACRYLATE SYNTHESIS

The synthesis of methyl methacrylate involves the following three steps:

(1) Synthesis of a propionate, in this case, propionic acid or propionic anhydride.
(2) Condensation of propionate with formaldehyde to produce methacrylic acid.
(3) Esterification of methacrylic acid with methanol to produce methyl methacrylate.

Two processes, one via propionic acid and one via propionic anhydride, are shown below, including a comparison of the current and novel routes (developed in this effort by Eastman Chemical) to produce the propionate (Step (1), above).

Methyl Methacrylate Synthesis Via Propionic Acid

Step 1. Synthesis of Propionic Acid

$H_2C{=}CH_2$ + CO + H_2 ==> CH_3CH_2CHO
(ethylene) (hydrogen) (propionaldehyde)

... **current** (1)

CH_3CH_2CHO + ½ O_2 ==> CH_3CH_2COOH
(propionaldehyde) (oxygen) (propionic acid)

$H_2C{=}CH_2$ + CO + H_2O ==> CH_3CH_2COOH ... **novel** (2)
(ethylene) (water) (propionic acid)

Step 2. Condensation of Propionic Acid with Formaldehyde

$EtCO_2H$ + HCHO ==> $CH_2{=}C(CH_3)COOH$ + H_2O (3)
(propionic acid) (formaldehyde) (methacrylic acid) (water)

Step 3. Esterification of Methacrylic Acid with Methanol

$CH_2{=}C(CH_3)COOH$ + CH_3OH ==> $CH_2{=}C(CH_3)COOCH_3$ + H_2O (4)
(methacrylic acid) (methanol) (methyl methacrylate) (water)

Methacrylic Acid Synthesis Via Propionic Anhydride

Step 1. Synthesis of Propionic Anhydride

2 $EtCO_2H$ + Ac_2O <==> AcOH + $(EtCO)_2O$ **... current** (5)
(propionic acid) (ac. anhydride) (ac. acid) (pr. anhydride)

$EtCO_2H$ + CO + $H_2C{=}CH_2$ ==> $(EtCO)_2O$ **... novel** (6)
(propionic acid) (ethylene) (pr. anhydride)

Step 2. Condensation of Propionic Anhydride with Formaldehyde

$(EtCO)_2O$ + HCHO ==> $CH_2{=}C(CH_3)COOH$ + $EtCO_2H$ (7)
(pr. anhydride) (formaldehyde) (methacrylic acid) (pr. acid)

Step 3. Esterification of Methacrylic Acid with Methanol

$CH_2{=}C(CH_3)COOH$ + CH_3OH ==> $CH_2{=}C(CH_3)COOCH_3$ + H_2O (4)
(methacrylic acid) (methanol) (methyl methacrylate) (water)

Note that reaction (7) produces both methacrylic acid and propionic acid in equimolar amounts. The propionic acid this produced would react further with formaldehyde (reaction (3)) to produce a second mole of methacrylic acid, which is then esterified (reaction (4)).

SYNTHESIS OF PROPIONATES

Minimizing the cost of propionate synthesis, and therefore that of methyl methacrylate (MMA), is a key part of the research since the first step in the generation of methacrylates is the generation of the propionate. Work thus far has focused on the development of a new highly active, low-cost, proprietary catalyst for this process which may replace existing catalysts, which are based upon either expensive Pt group metals (i.e., Rh) or the highly toxic nickel carbonyl. The initial focus has been the development of a propionic anhydride process based on the following reaction:

$$EtCOOH + H_2C{=}CH_2 + CO \Longrightarrow (EtCO)_2O \qquad (8)$$

The process is also amenable to the production of propionic acid and its esters using a similar chemistry. Typically, the reaction (8) above is performed at a pressure of 400-1000 psig and temperature of 140-200°C using a gas mixture consisting of ethylene and carbon monoxide which contains ca. 5-10% hydrogen (to maintain the catalyst in an active state).

The reaction has been observed to run at rates as high as 5-6 moles/L-h. However, at these high reaction rates, the reaction is mass transfer limited with the existing equipment. Most reactions in this study are run at slower reaction rates (typically in the range of 0.5 to 2.5 moles/L-h) to avoid this limitation. The reaction is carried out in a batch autoclave with a ratio of propionic acid to catalyst of 300-1200:1. Reaction rates are constant with time until conversions of 75-85% are achieved at which time the reaction rate decreases.

In-Situ Spectroscopic Probes. In-situ spectroscopic probes indicate the simultaneous presence of the following three catalyst phases under reaction conditions:

$M\text{-}CO$, $M\text{-}X^-$, and MX_2

where M = catalyst and X = an anionic component. Further studies indicate that the dominant phases, M-CO and $M\text{-}X^-$, are in equilibrium with each other as indicated in reaction (9) below:

$$M\text{-}CO + X^- \Longleftrightarrow M\text{-}X^- + CO \qquad (9)$$

In the absence of hydrogen, the entire catalyst is rapidly oxidized to MX_2, but the equilibrium mixture of reduced species is regenerated by the addition of hydrogen. Although the reaction proceeds in the absence of hydrogen, it is quite sluggish, and it usually stops prior to reaching high conversions.

Byproduct Determination. The reaction to form propionic anhydride is generally very selective, giving small quantities (<2%) of ethyl propionate, which is likely to be eventually converted to propionic anhydride in a continuous process. However, closer examination of byproducts by GC-MS reveals the presence of small quantities of 3-(4-hexanonyl) propionate (EtC(=O)CH(OOCEt)Et) and 5-ethyl-1-hydro-2-furanone (or an olefinic isomer thereof). These byproducts provide key insights into the reaction mechanism since both of these species represent reactions of a propionyl radical ($Et(CO)^\cdot$). The first product is coupling of the propionyl radical to form 3,4-hexanedione. The dione is a oxidant, and can be reduced by the components of the catalytic system to give 3-(4-hexanonyl) propionate, ultimately forming MX_2.

Kinetics. Kinetic studies have been run in the range of 0.5 to 2.5 moles/L-h to avoid the mass transfer related complications. To maintain consistent gas compositions in the head space of our reactor, a system equipped with a gas purge is used for the kinetic studies. We obtained the reaction rate orders on the catalyst level (M, in reaction (9) above), and the partial pressures of CO, EtX, X^-, hydrogen, and ethylene. These rate orders are:

Component	Experimental Reaction Order
M	0.62
EtX	0.54
X^-	1.00
CO	- 1.12
hydrogen	0.05* (*still under investigation).
ethylene	0.06

Mechanism. The mechanism of propionic anhydride formation from carbon monoxide, ethylene, and propionic acid has been formulated as follows:

$$^{\bullet}M(CO)^{-} + HX \implies {}^{\bullet}M(CO)^{-}H + I^{-} \qquad (10)$$

$$^{\bullet}M(CO)^{-}H + H_2C{=}CH_2 \implies (Et\text{-}M\text{-}CO)^{\bullet} \qquad (11)$$

$$(Et\text{-}M\text{-}CO)^{\bullet} + CO \implies (EtCO\text{-}M\text{-}CO)^{\bullet} \qquad (12)$$

$$(EtCO\text{-}M\text{-}CO)^{\bullet} + X^{-} \iff {}^{\bullet}(EtCOM\text{-}X)^{\bullet} + CO \qquad (13)$$

There is some evidence for the hydride process also since when the reaction is run in the absence of hydrogen, it is spontaneously evolved. If our catalyst follows the pathways described for catalysts such as Ir and Rh, it is likely that there are several pathways generating the catalyst-ethyl complex operating simultaneously (see P.R. Ellis, J.M. Pearson, A. Haynes, H. Adams, N.A. Bailey, and P.M. Maitlis, *Organometallics*, **13**, 3215(1994) and references cited therein.)

Refinements to the Kinetic and Mechanistic Model. Several probe reactions have been used to study the mechanism of the propionate synthesis catalyst. These studies are important in minimizing the cost of the propionate synthesis, and therefore that of MMA. Typical methylcyclopentanyl radical forming probes failed since isomerization of the olefinic-halide substrates was more rapid than the free radical initiation process. However, benzyl bromide proved to be a good probe. Using stoichiometric quantities of M(CO)X and benzyl bromide in diglyme and in absence of added CO, bibenzyl is the major product (from radical coupling). Equally important, significant quantities of phenylacetates, particularly benzyl phenylacetate and $PhCH_2CO_2CH_2CH_2OCH_2CH_2OCH_3$ (from reaction with solvent), are produced.

The presence of bibenzyl indicates that there are free radicals generated, but the presence of phenylacetates indicates that the free radicals may (and probably do) subsequently interact with the metal carbonyl complexes. This suggests that carbonylation of the radical likely occurs by subsequent attachment to a metal carbonyl, and not by direct carbonylation of the free radical as initially proposed since benzyl radicals are known to be refractory to direct carbonylation.

CONDENSATION CATALYSIS

Catalyst Synthesis. The synthesis of methyl methacrylate in one reactor depends on an active and selective catalyst for the condensation of formaldehyde with either propionic acid [reaction (3)] or propionic anhydride [reaction (7)]. The literature on the synthesis of methacrylic acid deals with the condensation of propionic acid and methyl propionate with formaldehyde [2, 4-8], and *not* with propionic anhydride. Because the anhydride route (a) does not prouce water (which can degrade the product and kinetically inhibit the reaction) and (b) produces a more easily separated product mix, initial efforts have focused on the catalytic condensation of propionic *anhydride* with formaldehyde [1]. However, the activity and selectivity of the catalysts developed here for the condensation of the anhydride must be compared to those for the acid to deteremine if the anhydride route [reactions (5)-(7) and (4)] is competitive with the conventional acid route [reactions (1)-(4)]. All the catalysts developed here are currently a matter of *patented proprietary information.*

Reported work on the condensation of propionic acid with formaldehyde can be divided into polymetal oxide catalysts, and other metal oxides on inert and active supports like the alkalized aluminas and silica-aluminas. Research on polymetal oxides is summarized in Table I.

Table I. Condensation of Propionic Acid with Formaldehyde on Polymetal Oxide Catalysts

Catalyst[1]	Atomic Ratio	Temp (deg C)	Yield (mol%)[2]
M_1-M_2-M_3	1/1.0	330	38
M_1-M_2-M_3	1/2/1.2	340	3
M_1-M_2-M_3	1/2/2.2	330	51
M_1-M_2-M_3	1/2/5.5	290	28
M_1-M_2-M_3	1/2/5.5	290	36
M_1-M_2-M_3	1/2/6.5	310	41
M_1-M_2-M_3	1/2/3.5	310	26
M_1-M_2-M_3	1/2/4.4	290	19
M_1-M_2-M_3	1/2/3.3	300	27
M_1-M_2-M_3	1/2/3.3	320	14

[1] M_1-M_2-M_3 are combinations of metal oxides; [2] Yield (mol%) of methacrylic acid based on charged HCHO, i.e., mole of methacrylic acid in the product/mole of HCHO charged x 100%; feed rates PA:HCHO:N_2 = 30-15-350 mmol/h; space velocity 448 cc/h/g-cat.

Based on Table I, at a 2:1 mole ratio of charged propionic acid to formaldehyde, the maximum yield of methacrylic acid based on charged HCHO is about 50%. [At the 2:1 feed ratio of propionic acid to formaldehyde, this corresponds to a 25% yield based on propionic anhydride charged.] The conversion of HCHO under these conditions is about 80%.

Catalysts other than poly metal oxide catalysts have also been tested for the condensation of propionic acid and formaldehyde. Results are summarized in Table II.

Based on Table II, the maximum yield of methacrylic acid based on charged HCHO is ca. 60% (corresponding to 30% yield based on charged propionic acid). Maximum conversions of propionic acid and formaldehyde are ca. 40% and 70%, respectively. However, unlike the results shown in Table I, these results are for a wide range of space velocities.

Table II. Catalyst Performance for Condensation of Propionic Acid with Formaldehyde, Supported Metal Catalysts

Catalyst	PA/HCHO[1] mol ratio	PA Conv. (%)	HCHO Conv. (%)	MAA Yield mol% on PA	MAA Yield mol% on HCHO
M/SiO_2	10	-	68.0	5.4	54.3
M/SiO_2	1.0	34.0	39.0	24.1	24.1
M/SiO_2	1.0	24.1	-	13.3	13.3
M/SiO_2	1.5	32.1	-	10.0	29.3
M/Al_2O_3	0.5	27.3	-	23.3	11.7
M_1+M_2/SiO_2	0.5	33.7	-	27.8	13.9
M_1+M_2/SiO_2	1.5	40.7	61.3	31.5	47.2
$M_{1x}M_{2y}$	2.0	38.1	-	31.3	62.4
$M_{1x}M_{2y}$	1.4	40.0	-	33.1	44.8

[1] PA = propionic acid, HCHO = formaldehyde, MAA = methacrylic acid. Reaction Conditions ca.: T = 300-350 °C, N_2(carrier)/PA mol ratio = 10-20.

These results provide a basis of comparison for catalysts developed in this work for thecondensation of propionic *anhydride*. Again, catalysts developed here are subject of *patented proprietary information.* The catalysts shown in Table III were studied here for the condensation of the anhydride. The catalysts from groups A, B, C, F, and G were prepared by the incipient wetness technique [3, 9]. The catalysts from groups D were prepared by co-precipitation. Catalysts from group E were synthesized by gel precipitation.

TABLE III. Summary of Condensation Catalysts for MAA Synthesis

Catalyst Group	Support	Additive(s)
A	Alumina	metals
B	Aluminosilicates	metals
C	Silica	metals
D	Silica	mixed metals
E	Titania	mixed metals
F	Silica	mixed metals
G	Magnesia	mixed metals

Characterization of Condensation Catalysts. The catalysts have been analyzed for metal content by inductively coupled plasma - optical emission spectrometry (ICP-OES). The catalysts from groups D, E, and F are observed to be amorphous, based on x-ray powder diffraction. The B.E.T. - N_2 surface area on a typical polymetal oxide synthesized in our laboratory is ca. 96 m^2/g. Pore size distribution and average pore size determination is currently in progress. This polymetal oxide is used to generate the reaction rate data, in terms of methacrylic acid yield and reactant conversions, summarized in Table V.

Catalyst Testing. The catalysts were tested for their condensation activity in a bench-scale gas-phase microreactor system. All tests thus far have been made on the condensation of propionic anhydride with formaldehyde, reaction (7) above. The reaction conditions are:

- T = 400 °C and 300 °C
- P = 2 atm
- F/W = 290-1200 cc/h/g-cat

A flow diagram of microreactor system is shown in Figure 1.

Results at 400 °C showed that propionic anhydride undergoes significant decarboxylation, forming carbon dioxide and 3-pentanone (diethyl ketone), as reported in the literature. Other results at 400 °C showed that our proprietary catalysts are active for methacrylic acid synthesis. Initial tests at 300°C have focused on a polymetal oxide catalyst with a specified atomic ratio. The results are summarized in Table IV . [Further tests on the catalysts are planned, including long term runs to examine the possible effect of changes in surface acidity on methacrylic acid yield.] The maximum yield of methacrylic acid, based on HCHO, is 77% at 290 cc/h/g-cat. At 1200 cc/h/g-cat, the yield on the same basis is 65%.

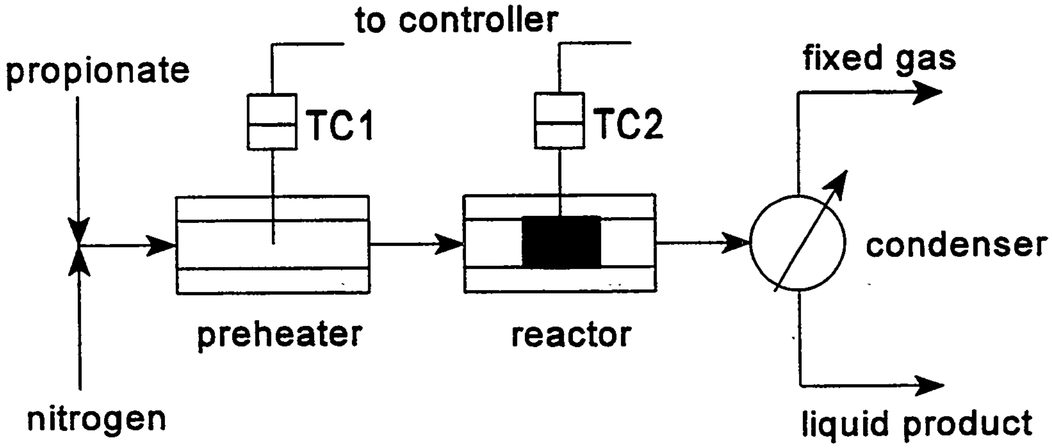

Figure 1. Schematic of Experimental Microreactor System.

Table IV. Condensation of Propionic anhydride with Formaldehyde[1]

Space velocity, cc/h/g-cat	PA Conv.[2]	MAA yield[3]	MAA yield[4]	MAA rate[5]	C balance on liquid products[6]
480	42.6%	36.4%	16.7%	0.868	83.5%
290	44.8%	76.8%	36.4%	1.251	88.2%
1200	43.8%	65.3%	30.6%	0.887	79.3%
900	28.2%	30.1%	14.1%	1.226	86.7%

[1] Reaction conditions: T = 300 C, P = 2 atm (30 psi in-house nitrogen), mole flow rates of propionic anhydride:formaldehyde:nitrogen = 40:20:220 mmol/h.
[2] Propionic acid conversion, (mol PAC out - 2 x mol PAN in) / (2 x mol PAN in) x 100.
[3] MAA yield based on charged HCHO, i.e., mol MAA/mol charged HCHO x 100.
[4] MAA yield based on charged propionic anhydride
[5] MAA rate, gmol/kg cat. h.
[6] The carbon balance reported here accounts for only the liquid products collected in a condenser downstream of the reactor. CO, CO_2, and unreacted formaldehyde are detected in the exit gas also, but are not quantified here.

A comparison of the results reported in the literature for the condensation of propionic acid and those for the anhydride in this study are shown in Table V.

Table V. Comparison of Catalysts for Condensation of Propionic Acid and Anhydride[1]

Space velocity, cc/h/g-cat	Catalyst (atomic ratio for M_1-M_2-M_3)	Temp, °C	PA/HCHO	PAA/ HCHO	MAA yield, based on HCHO	MAA yield, based on PA	MAA yield, based on PAA
448	x_1-x_2-x_3	330	2:1	—	51	25	—
NA	x_1-x_2-x_3	300-350	10:1	—	54	5.4	—
290	x_1-x_2-x_3	300	—	2:1	77	—	36
1200	x_1-x_2-x_3	300	—	2:1	65	—	31

[1] PA=propionic acid, PAA=propionic anhydride, MAA=methacrylic acid

These results, for catalysts that have not been fully characterized or optimized, show that yields of methacrylic acid from propionic anhydride are comparable and in some cases even superior to those reported in the literature for the acid. The yields do not approach, yet, to those likely needed for a commercially practical process, however. Further improvements in the yield, selectivity, and long-term activity are possible after a complete catalyst characterization and optimization, particularly in terms of the acid-base properties. These crucial studies constitute the focus of ongoing research effort.

SUMMARY

The development of a syngas-based process for the synthesis of methyl methacrylate depends on:

- the development of a cost-competitive process for the propionate. We have focused on the anhydride because of it produces a more easily separated product mix and eliminates a mole of water, which is a kinetic inhibitor.
- the development of an active and selective condensation catalyst for the anhydride.

Experimental results show that:

- the synthesis of propionic anhydride (via the acid) can be achieved using homogeneous catalysts for the reaction of ethylene, CO, and steam. The reaction appears to be a free radical process and hydrogen is needed to maintain the catalyst in a reduced state.
- the condensation of the anhydride can be catalyzed by catalysts based on those reported for the condensation of the acid, with comparable yields. Further improvements in these yields are needed for the process to produce methyl methacrylate to be commercially viable.

- We are developing a novel environmentally-benign cost-competitive process for the synthesis of methacrylates from syngas.
- Propionic anhydride is selected as the target propionyl intermediate moiety.
- The direct synthesis of propionic anhydride from propionic acid and ethylene (and hydrogen in some cases) is the most promising and economical route for propionic anhydride synthesis.
- Several amphoteric and acid catalysts have been tested in a bench-scale microreactor system for their activity in methacrylic acid synthesis from propionic anhydride and formaldehyde. The yield of methacrylic acid is 77% (based on charged HCHO) and a space velocity of 290 cc/h/g-cat, and 65% at 1200 cc/h/g-cat, which is comparable to that reported in the literature for the condensation of the acid.

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