

SYNTHESIS OF METHYL METHACRYLATE (MMA) VIA C₂-CARBONYLATION AND C₃-CONDENSATION REACTIONS

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INTRODUCTION

The most widely practiced commercial technology for the synthesis of methacrylic acid (MAA) and methyl methacrylate (MMA) is the acetone cyanohydrin (ACH) process. The ACH process requires handling of large quantities of extremely toxic and hazardous hydrogen cyanide and generates copious amounts of ammonium sulfate wastes which are either discarded or reclaimed at substantial cost. The ACH technology is thus environmentally and economically untenable for new expansions. There is a strong drive within the chemical industry for an alternate coal-based process (Gogate et al., 1997; Spivey et al., 1995a, 1996). The process proposed here (Figure 1) is based on C₂-hydrocarbonylation reactions using CO generated from coal and C₃-Condensation reactions (Spivey et al., 1995b) and consists of three steps: Step 1—ethylene carbonylation, Step 2—formaldehyde condensation, and Step 3—esterification of MAA produced in Step 2 to MMA. Steps 1 and 2 present technical challenges for successful commercial demonstration and are the focus of this paper.

The research presented in this paper on Step 1 elucidates the development of a homogeneous catalyst for propionate synthesis and research on Step 2 delineates the development of an acid-base catalyst for condensation of formaldehyde with propionates. Additionally, results of a preliminary economic analysis comparing the product value of MMA via six different commercial or near-commercial routes is presented.

EXPERIMENTAL

Ethylene Carbonylation

To allow the measurement of experimental rates of ethylene carbonylation to propionates, a 2-L Hastelloy[®]-C overhead stirred autoclave was fitted with a high-pressure condenser and a dip tube for removing samples during the reaction. During a typical run, 5.81 g (0.022 mol) of Mo(CO)₆, 15.5 g (0.040 mol) of tetrabutyl phosphonium iodide, 109.2 g (0.700 mol) ethyl iodide, 81 g (4.5 mol) of H₂O, and 450 g (7.5 mol) of acetic acid (as an internal standard and solvent) were added to the autoclave. The autoclave was then pressure-tested with nitrogen at 68.0 atm and a gas purge was established through the reactor at 3 mol/h. The nitrogen was vented, and autoclave was then pressurized to 23.8 atm with 5 percent hydrogen in carbon monoxide, and subsequently heated to 160 °C. Upon reaching the temperature, the pressure was raised to 51.0 atm using a gas mixture consisting of 6 percent hydrogen, 47 percent CO, and 47 percent ethylene, maintaining the 3 mol/h gas purge. Liquid samples were removed every 30 min from the reactor for the first 5 hours after the steady state was reached, and analyzed for ethyl iodide, ethyl propionate, acetic acid, and propionic acid, using a Hewlett Packard 5890 Gas Chromatograph (GC) containing a 25 m (0.25 - mm ID, 0.25 μm film) Quadrex 007 FFAP capillary column, with p-xylene as the internal standard. Gas samples were also removed every 60 min for first 5 h, to ensure that the gas composition was uniform. All trace materials were detected by a gas chromatograph (GC) / mass spectrometer (MS).

Condensation Catalysis

The condensation catalysts were tested in a continuous fixed-bed microreactor system. The nominal flow rates of propionic acid, formaldehyde, and nitrogen were kept at 75, 15, and 220 mmol/h. The feed was prepared by dissolving trioxane (solid trimer of formaldehyde) into propionic acid in a ca. 5:1 mole ratio, and fed into a preheater maintained at 300 °C, using a syringe pump (ATI Orion SAGE M361). The vaporized feed was passed over a catalyst charge, located centrally in a 6-mm ID x 356-mm L SS316 reactor tube. The catalyst charge (of a 16-30 mesh nominal size fraction) was held in place by glass wool and glass beads. Thermocouples mounted directly at the entrance and exit of catalyst bed provided temperature control and readout. Both the preheater and the reactor

were mounted horizontally in Lindberg furnaces (Blue M, Model #TF55035A). The product vapors containing methacrylic acid, water, propionic acid, and diethyl ketone were cooled and collected in a impinger contained in an ice bath. The product gases were collected in a Tedlar Bag. The liquid products were analyzed over a fused silica capillary column (30 m x 0.32 mm ID) with a 0.25 µm film thickness of DB-FFAP, using a flame ionization detector (FID) using a HP 5890 gas chromatograph (GC). The gas samples were analyzed using a fixed-volume loop injection onto a Poropak[®]T/Molecular Sieve (MS) 5 Å columns, with a column isolation sequence, using a thermal conductivity detector (TCD).

The catalysts were characterized for their surface area, pore volume, and surface acid-base properties. The surface and pore volume determinations were made on a Quantachrome NOVA 100 BET-N₂ surface area analyzer. The acid-base properties were measured on an Altamira AM1-100 catalyst characterization system. The NH₃-adsorption was carried out with a 10 percent NH₃-N₂ gas mixture (25 mL/min) for 30 min at 50 °C. The desorption was carried out from 50 to 550 °C, at 10 °C/min. The evolved gases were continuously monitored using a thermal conductivity detector (TCD). For surface basicity measurements, an identical time, temperature, and flow profile was followed, with a 10 percent CO₂-N₂ gas mixture as the treatment gas.

RESULTS AND DISCUSSION

Ethylene Carbonylation.

General Description of the Catalyst. Although homogeneous catalysts for this reaction are well known (Samel et al., 1993), commercial application has been limited to a highly toxic and volatile Ni(CO)₄ catalyst operating at high pressures (>180 atm) and high temperatures (>270 °C) (Bertleff, 1986; Samel et al., 1993) to produce propionic acid. Processes operating at lower pressures and temperatures generally require expensive catalysts such as Rh, Ir, or Pd and none have been employed commercially (Bertleff, 1986; Colquhoun et al., 1991; Forster et al., 1981; Mullen, 1980; Pino et al., 1977). Although Cr group metals have been used in combination with known carbonylation catalysts such as Co, Ni, Rh, and Ir, they have not been shown to have significant catalytic activity in isolation. In the study reported here, a halide-stabilized Mo(CO)₆ homogeneous catalyst is used at 130 to 170 °C and 350 to 750 psig.

The results of batch experiments comparing the observed order of reactivity for the Group 6 metals shows that Mo>>W>Cr and that the halide employed may be either Br or I. Substitution of bromine for iodine only leads to a small change (~25 percent decrease) in reaction rate, suggesting an electron transfer process (Huber et al., 1995). When the process is operated with a catalyst composed of Bu₄PI, Mo(CO)₆, and EtI, the Mo catalyzed carbonylation of ethylene to propionic anhydride at a nearly linear rate with time, until a 75- to 85-percent conversion of the propionic acid is achieved, at which point the reaction begins to slow markedly. A typical reaction profile for this process appears in Figure 2.

Effect of Temperature, Determination of Activation Parameters. The effect of temperature was measured in batch experiments between 130 and 170 °C using identical levels of gas and catalyst components throughout the full range of temperatures. The apparent activation energy (E_{app}) was 39.3 kcal/mol. The rate expression is:

$$k = \frac{\text{Rate} \cdot [P_{T_2}]^{0.58}}{[\text{Mo}(\text{CO})_6]^{0.6} [\text{EtI}]^{0.6} [\text{I}^-]}$$

The enthalpy of activation (ΔH[‡]) and entropy of activation (ΔS[‡]) were determined from the Eyring plot: [ln (k/T vs. 1/T)] ΔH[‡] was found to be +38.4 kcal/mol and ΔS[‡] was estimated to be +40 cal/mol/K. These activation parameters suggest a rate-determining step involving the dissociation of the Mo-CO bond in Mo(CO)₆ (Ehlers and Frenking, 1993, 1994).

Kinetic Effects of Reactants. To measure kinetic effects due to ethylene, CO, and hydrogen, a continuously gas purged autoclave with a liquid sampling loop was used. Using this apparatus, the partial pressure of each reactant could be varied independently. The effects of hydrogen and ethylene were uneventful and increasing partial pressures of these two reactants did not show any discernible increase in the reaction rate. It was therefore concluded that the reaction is zero order with respect to hydrogen and ethylene. Increasing the partial pressure of CO led to a decreased reaction rate and the measured reaction order was found to be -1.2. This inverse and complex dependence of reaction order in CO suggests that the overall mechanism involves a step which is inhibited by CO. To study the effect of Mo(CO)₆, EtI, and Bu₄I levels on reaction rate, the partial

pressures of CO, hydrogen, and ethylene were kept constant, with CO levels controlled very accurately at 23.8 atm. While the reaction order in Bu₄I was first order, the experimentally measured reaction orders for both Mo(CO)₆ and EtI were both approximately 1/2 order, indicating a likely free-radical type reaction mechanism. Based on these reaction order measurements, a predictive rate equation was proposed.

Condensation Catalysis

The condensation of formaldehyde with propionic acid is catalyzed by acid-base catalysts, as shown in Figure 3 (Gogate et al., 1997). The catalyst development effort has focused on developing a stable, selective, and active condensation catalyst for this reaction. Fixed-bed microreactor studies of more than 80 potential catalytic materials have shown that Group V metals (V, Nb, and Ta) are active condensation catalysts and that niobium catalysts are the most active.

The results show that the 20 percent Nb/SiO₂ is the most active catalyst. However, the catalyst deactivates. The long-term deactivation of a 10 percent Nb/SiO₂, V-Si-P 1:10:2.8, and 10 percent Ta/SiO₂ are shown in Figure 4. The deactivation of these catalysts has been correlated with the strength and distribution of the acid and base sites on the catalyst. There appears to be an optimum balance between these sites that is necessary to promote the condensation reaction. Figure 4 shows that an oxidative treatment of the deactivated catalyst partially restores the activity. Work is under way to minimize deactivation.

Economics of the Overall Process

An economic analysis was carried out by Eastman and Bechtel based on the results on the 20 percent Nb/SiO₂ catalyst at 300 °C, 2 atm, flow rates of propionic acid: formaldehyde:nitrogen 72:16:200 mmol/h, 5 g catalyst charge (0.7- to 1.1-mm size fraction), and a volume hourly space velocity of 1,080 cm³/g cat·h. Reaction kinetics are assumed to be first order in formaldehyde, in order to remove the effects of excess nitrogen diluent and excess HOPr. This process was compared to five commercial (or, near commercial) technologies for MMA manufacture:

- Conventional ACH-based process (Rohm & Haas),
- (New) Mitsubishi Gas Chemical (MGC) ACH-based process,
- *i*-butylene oxidation process (Lucky, Japan Methacrylic),
- *t*-butanol oxidation process (Kyodo, Mitsubishi Rayon), and
- Propyne carbonylation (Shell, ICI).

A comparison of production cost (or, product value) was carried out for these six routes, based on a 250 Mlb/year plant (except for the propyne carbonylation process, for which a 100 Mlb/year capacity is assumed due to the very limited worldwide supply of propyne). To account for catalyst deactivation, the process design includes parallel fixed-bed reactors.

The product value comparison for the RTI-Eastman-Bechtels HOPr/MeOH route with five commercial routes (Figure 5) shows that the RTI-Eastman-Bechtels three-step process at 52¢/lb MMA is competitive with all commercial technologies for MMA manufacture, except propyne carbonylation (at 44¢/lb). [The current selling price for MMA is roughly 75¢/lb.] However, the propyne carbonylation technology suffers from limited raw material supply. Both the conventional ACH and MGC ACH-based processes (at 73¢/lb and 70¢/lb MMA, respectively) are more costly than the RTI-Eastman-Bechtels three-step route, as is the *i*-butylene oxidation route (at 59¢/lb). In the United States, the *i*-butylene route suffers from competing raw material demands for methyl tert-butyl ether (MTBE) plants. The *t*-Butanol oxidation process at 55¢/lb MMA appears quite competitive with the RTI-Eastman-Bechtels three-step process.

CONCLUSIONS

The carbonylation of olefins, particularly ethylene, with a halide-promoted Mo catalyst represents the efficient process using a Cr-group metal as the active catalyst. Detailed mechanistic analysis indicates that the reaction likely proceeds via a free radical mechanism, which is initiated by a rate limiting dissociation of CO from Mo(CO)₆. The precise propionate derivative obtained depends on the nature of the nucleophile, and the process for propionic acid uses steam. If present in too large a quantity (alcohol for methyl propionate process, or water for propionic acid process), the nucleophilic component can inhibit the reaction, by competing with the EtI for the vacant coordination site of Mo(CO)₆. The condensation of propionate derivatives with formaldehyde is a synthetic route to MAA and MMA. The reaction mechanism suggests that both acid and base properties are required and a definitive balance of acid and base site strengths is perhaps needed for an active, selective, and stable catalyst. As a result of screening over 80 catalytic materials, a 20%

$\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst is found to give optimum performance, although catalyst deactivation is ubiquitous on this and other catalysts. Detailed XPS/ESCA/XRD studies prove that carbon deposits in nodular form on the active Nb_2O_5 sites, thereby limiting accessibility of an Nb_2O_5 site to the reactants. Based on the XPS/ESCA study of a regenerated catalyst (using oxidative regeneration), a reaction-regeneration cycle study on the 20% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ is planned, which may alleviate the catalyst deactivation pattern. A preliminary economic evaluation of the RTI-Eastman-Behcetel three-step methanol process consisting of external formaldehyde generation, condensation of formaldehyde with propionic acid, and external esterification of resulting methacrylic acid with methanol to form MMA shows that for a 250 Mlb/yr product and 10 percent rate of return on investment, the product value of RTI-Eastman-Behcetel three-step route at 52¢/lb is cost-competitive with known commercial and near commercial technologies for MMA manufacture, except propyne carbonylation, which suffers from limited raw material supply. Further research on condensation catalysis, particularly in enhancing catalyst longevity is under way.

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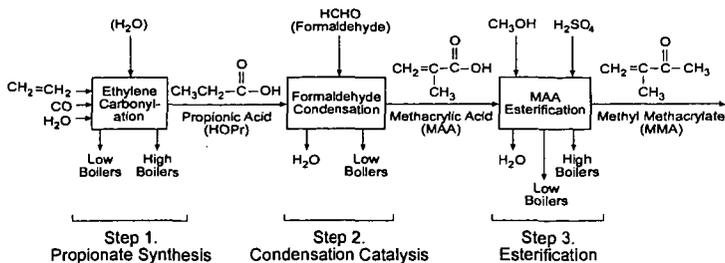
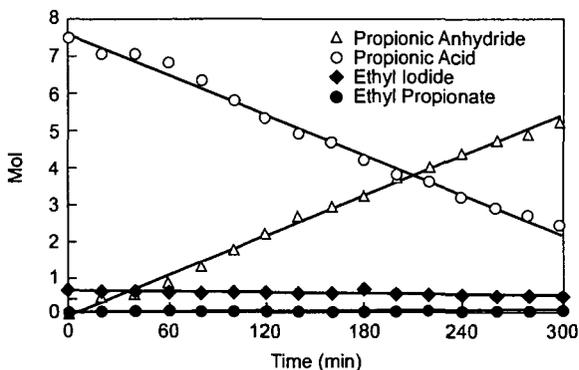


Figure 1. RTI-Eastman-Bechtel three-step HOPr/MeOH-based MMA process (with external formaldehyde feed).



Initial composition: EtI, 0.7 mol; EtCOOH, 7.5 mol; Mo(CO)₆, 22 mmol; Bu₄PI, 40 mmol. Conditions: 160 °C, 55 atm. Gas compositions: 5% H₂, 50% C₂H₄, 45% CO.

Figure 2. Reaction profile for the carbonylation of ethylene to propionic anhydride.

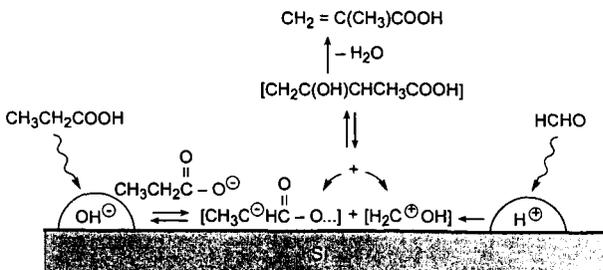
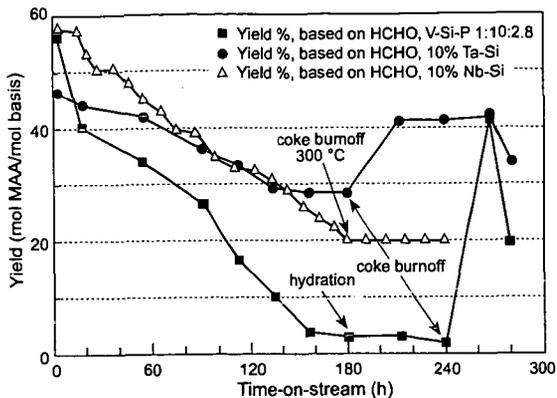


Figure 3. Representative mechanism for propionic acid and formaldehyde.



Experimental Conditions V-Si-P, Ta-Si

For V-Si-P, Ta-Si: 300 °C, 2 atm, 15 g cat. charge, 41:17:220 mmol/h
 PAA:HCHO:Nitrogen, 290 cm³/g cat-h

For Nb/Si: 300 °C, 2 atm, 5 g cat. charge, 72:16:220 mmol/h
 PA:HCHO:Nitrogen, 1080 cm³/g cat-h

Figure 4. Long-term activity check on V-Si-P 1:10:2.8, 10% Ta-Si, and 10% Nb-Si catalysts.

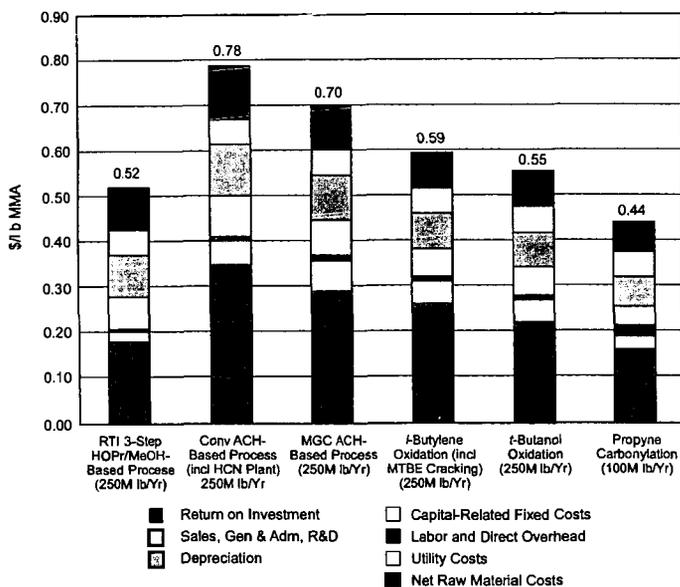


Figure 5. MMA processes, product value comparison (10% ROI).