SYNTHESIS OF METHYL METHACRYLATE FROM COAL-DERIVED SYNGAS

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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. About 6 billion pounds of MMA are produced annually, corresponding to roughly $4.5 billion in sales. 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 currently environmentally and economically untenable for any new expansions. There is a strong drive within the chemical industry for a process that is based on domestically produced coal-derived syngas (Gogate et al., 1996; Spivey et al., 1995a, 1996). The process proposed here (Figure 1) is based on $C_2^=$-hydro-carbonylation using CO generated from coal (Spivey et al., 1995a, 1995b; McKetta, 1989). Note: This process consists of three steps: Step1–ethylene carbonylation, Step 2–formaldehyde condensation of the C_3 produced in Step 1 to produce MAA, and Step 3–esterification of MAA to MMA. Step 3 is known art. Steps 1 and 2 present technical challenges for successful commercial demonstration and are the focus of this project.

The research on Step 1 is focused on two tasks: (1) development of a homogeneous catalyst for propionate synthesis, and (2) preliminary design and economic analysis.

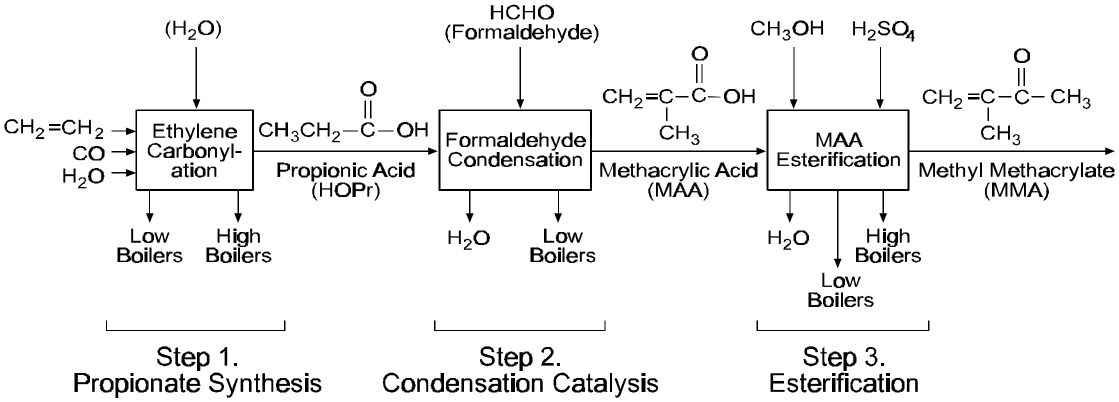


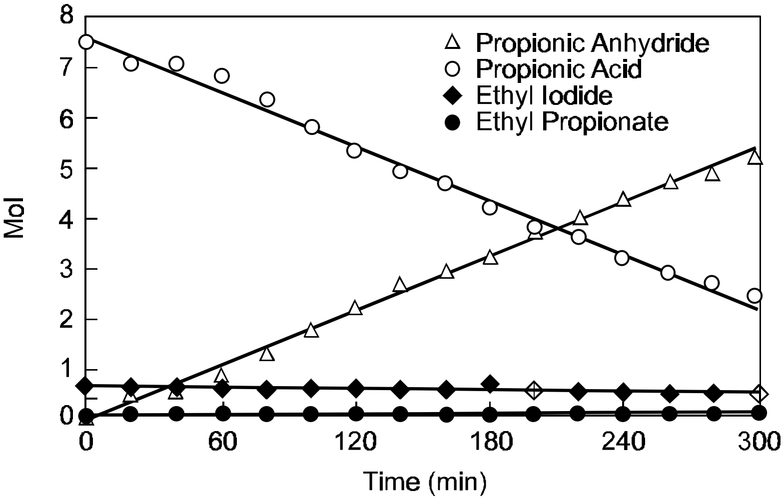
Figure 1. RTI-Eastman-Bechtel three-step HOPr/MeOH-based MMA process (with external formaldehyde feed).

The research on the second step also consists of two tasks: (1) development of an acid-base catalyst for condensation reaction, and (2) development of combined methanol partial oxidation-condensation catalyst for one-step MMA synthesis.

RESULTS AND DISCUSSION

Step 1. Ethylene carbonylation. 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 Bu_4PI, $Mo(CO)_6$, 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.



Initial composition: EtI, 0.7 mol; EtCOOH, 7.5 mol; $Mo(CO)_6$, 22 mmol; Bu_4PI, 40 mmol. Conditions: 160 °C, 55 atm. Gas compositions: 5% H_2, 50% C_2H_4, 45% CO.

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

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_{act}) was 39.3 kcal/mol. The rate expression is:

$$k = \frac{\text{Rate}\cdot[P_{co}]^{1.17}}{[\text{Mo(CO)}_6]^{0.62}[\text{EtI}]^{0.52}[\text{I}^-]} .$$

The enthalpy of activation (ΔH‡) and entropy of activation (ΔS‡) were determined from the Eyering plot: [ln (k/T vs. (l/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).

Step 2-Condensation. 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.

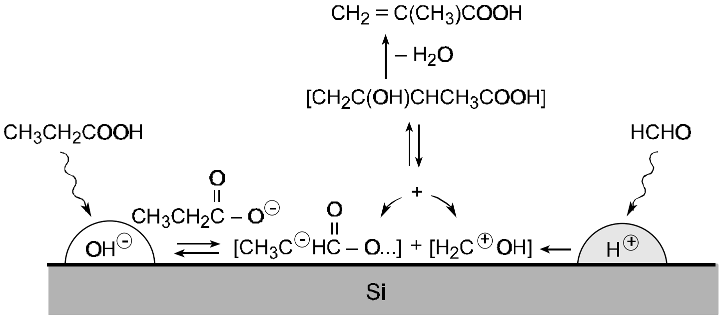
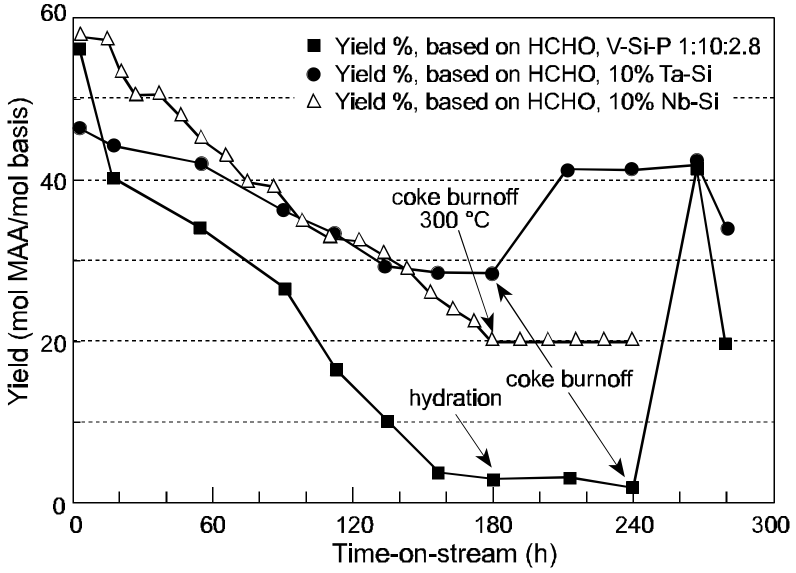


Figure 3. Representative mechanism for propionic acid and formaldehyde.

The results show that the 20 percent Nb/SiO_2 is the most active catalyst. However, the catalyst deactivates. The long-term deactivation of a 10 percent Nb/SiO_2, V-Si-P 1:10:2.8, and 10 percent Ta/SiO_2 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 5 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/SiO_2 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 cm^3/g cat·h. Reaction kinetics are assumed to be first order in formaldehyde. This process was compared to five 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).



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 cm^3/g cat•h

For Nb/Si: 300 °C, 2 atm, **5 g cat. charge**, 72:16:220 mmol/h
PA:HCHO:Nitrogen, 1080 cm^3/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.

A comparison of capital cost, production cost (or product value), and the sensitivity of capital cost and product value to capacity was carried out 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.

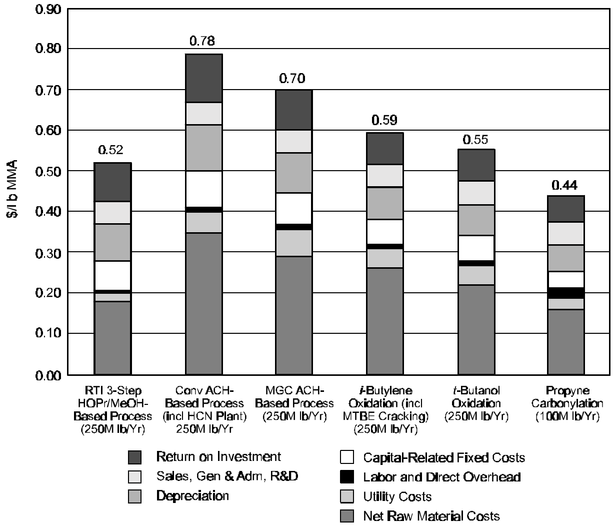


Figure 5. MMA processes, product value comparison (10% ROI).

The product value comparison for the RTI-Eastman-Bechtel HOPr/MeOH route with five commercial routes (Figure 5) shows that the RTI-Eastman-Bechtel 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 and is not likely to be a commercial technology in the United States. Both the conventional ACH and MGC ACH-based processes (at 73¢/lb and 70¢/lb MMA, respectively) are more costly than the RTI-Eastman-Bechtel three-step route, as is the *i*-butylene oxidation route (at 59¢/lb). In the United States, the *i*-butylene route is not likely to be commercial because of the raw material demands for methyl tert-butyl ether (MTBE) plants. *t*-Butanol oxidation process at 55¢/lb MMA appears quite competitive with the RTI-Eastman-Bechtel three-step process.

A sensitivity study carried out by Eastman (Figure 6) shows that the greatest uncertainty is in the capital cost. The reaction rate (g MAA/kg cat·h), raw material price (formaldehyde, methanol, and ethylene) and MAA selectivity also have a pronounced effect on the MMA product value.

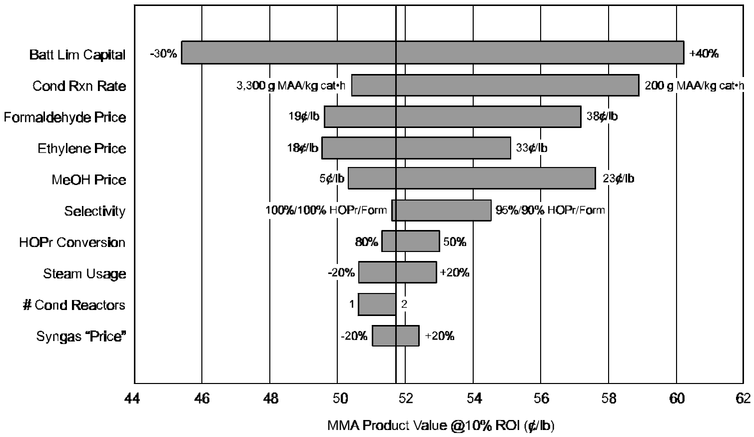


Figure 6. RTI-Eastman-Bechtel three-step HOPr/MeOH-based MMA process-sensitivity study.

For example, at a nominal reaction rate of 200 g MAA/kg cat·h (corresponding to that of the catalyst 20 percent Nb/SiO_2 catalyst), the MMA product value is 58¢/lb; however, at a reaction rate of 3,300 g MAA/kg cat·h (assuming first-order reaction in propionic acid, first order in formaldehyde, no nitrogen diluent, PA/HCHO= 1.5), the MMA product value decreases to about 50¢/lb. Thus, even with the current unoptimized catalyst, the RTI-Eastman-Bechtel three-step process is cost-competitive with all other commercial technologies for MMA manufacture. Even though the current catalyst does deactivate, the sensitivity of the product value to the number of condensation reactors (1 or 2) is minimal. To make these economic assertions more sound, knowledge gaps including catalyst deactivation, intrinsic reaction kinetics, and formaldehyde generation and recovery need to be addressed.

FUTURE WORK

- ***Long-term catalyst activity***—effect of various promoters on catalyst life will be examined and possible beneficial effects of oxygen co-feed and reaction-regeneration cycles to maintain the catalyst activity will also be studied.

- ***Catalyst structure***—The structure of the niobium catalyst will be studied in greater detail to elucidate the difference in physical and chemical properties of the fresh and deactivated catalysts.

- ***Intrinsic kinetics***—Eastman's economic analysis assumed a first-order kinetics in formaldehyde. Activation energy, temperature, and concentration dependence of the MAA reaction rate will be determined. The MAA reaction rate is the single most important parameter affecting the MMA product value, based on Eastman's analysis.

CONCLUSIONS

A preliminary economic evaluation of the RTI-Eastman-Bechtel 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. The results show that for a 250 Mlb/yr product and 10 percent rate of return on investment, the product value of RTI-Eastman-Bechtel three-step route is at 52¢/lb and is cost-competitive with all 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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