

Synthesis of Methyl Methacrylate From Coal-Derived Syngas

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ABSTRACT

Research Triangle Institute (RTI), Eastman Chemical Company, and Bechtel collectively are developing a novel three-step process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas that consists of the steps of synthesis of a propionate, its condensation with formaldehyde to form methacrylic acid (MAA), and esterification of MAA with methanol to produce MMA. RTI has completed the research on the three-step methanol-based route to MMA. Under an extension to the original contract, RTI is currently evaluating a new DME-based process for MMA. The key research need for DME route is to develop catalysts for DME partial oxidation reactions and DME condensation reactions.

Over the last quarter (April-June, 1998), RTI has modified the reactor system including a new preheater and new temperature settings for the preheater. Continuous condensation of formaldehyde with propionic acid were carried out over 10% Nb₂O₅/SiO₂ at 300°C without interruption. Five activity and four regeneration cycles have been completed without plugging or material balance problems. The results show that 10% Nb₂O₅/SiO₂ deactivates slowly with time but can be regenerated, at least four times, to 100% of its original activity with 2% O₂ in nitrogen at 400°C. The cycles continue with consistent 90-95% of carbon balance. The reaction is scheduled to complete with 6 activity cycles and 5 regenerations. Used catalysts will be analyzed with TGA and XPS to determine bulk and surface coke content and coke properties. RTI will start the investigation of effects of propionic acid/formaldehyde ratio on reaction activity and product selectivity over 20% Nb₂O₅/SiO₂ catalysts.

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LIST OF ABBREVIATIONS

ACH	Acetone cyanohydrin
DME	Dimethyl ether
DOE	U.S. Department of Energy
ESCA	Electron spectroscopy for chemical analysis
MAA	Methacrylic acid
MMA	Methyl methacrylate
MP	Methyl propionate
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

EXECUTIVE SUMMARY

The Research Triangle Institute (RTI)-Eastman-Bechtel team is developing a novel process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas. The three-step process consists of synthesis of a propionate, its condensation with formaldehyde to produce methacrylic acid (MAA), and esterification with methanol to yield MMA. As an extension to the original contract, RTI is currently working on the evaluation of a dimethyl ether (DME)-based process. In this evaluation, DME is used as a source of formaldehyde, and methyl propionate (MP) is used as the propionyl source. The key research need for a DME-based process is to develop catalysts for DME partial oxidation reactions and DME condensation reactions.

Over the last quarter (April-June, 1998), RTI has modified the reactor system including a new preheater and new temperature settings for the preheater. Continuous condensation of formaldehyde with propionic acid were carried out over 10% Nb₂O₅/SiO₂ at 300°C without interruption. Five activity and four regeneration cycles have been completed without plugging or material balance problems. The results show that 10% Nb₂O₅/SiO₂ deactivates slowly with time but can be regenerated, at least four times, to 100% of its original activity with 2% O₂ in nitrogen at 400°C. The cycles continue with consistent 90-95% of carbon balance. The reaction is scheduled to complete with 6 activity cycles and 5 regenerations. Used catalysts will be analyzed with TGA and XPS to determine bulk and surface coke content and coke properties. RTI will start the investigation of effects of propionic acid/formaldehyde ratio on reaction activity and product selectivity over 20% Nb₂O₅/SiO₂ catalysts.

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 that are either discarded or reclaimed at substantial cost. The ACH technology is currently environmentally and economically untenable for any new expansions, primarily because of the cost of either disposing or regenerating the bisulfate waste.

There is a strong drive within the chemical industry for a replacement process for MMA synthesis (Gogate et al., 1997; Spivey et al., 1998, 1997a, 1997b). The Research Triangle Institute (RTI)-Eastman-Bechtel research team is developing a novel three-step process for synthesis of methyl

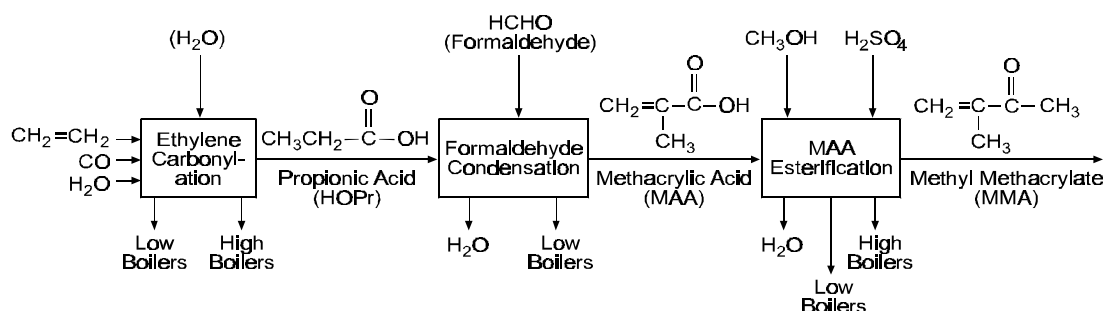


Figure 1. The RTI-Eastman-Bechtel three-step MMA process (with external formaldehyde feed).

methacrylate from coal-derived syngas. This three-step process is shown schematically in Figure 1. In this process for MMA manufacture, Steps 1 (ethylene carbonylation) and 2 (formaldehyde condensation), present challenges for successful commercial demonstration of the process. Step 3 (MAA esterification) is a known art.

The three-step methanol route has been investigated by the RTI-Eastman-Bechtel research team. For investigation purposes, the scope of work was divided into three tasks. Task 1 focused on the synthesis of a propionate from ethylene, CO, and steam, Task 2 focused on the condensation of the propionate with formaldehyde, and Task 3 focused on the one-step oxidative condensation in a slurry reactor. Due to a promising economic evaluation of the three-step process, where propionate synthesis, condensation, and esterification are carried out in separate reactors, the development of one-step MMA process in a slurry reactor (Task 3), was de-emphasized, for now. Upon conclusion of the original contract, the RTI-Eastman-Bechtel research team undertook the development of a DME-based process to MMA, as an extension to the three tasks of the original contract. This add-on task was called as Task 4, and termed as DME feedstock evaluation.

Under this extension, the RTI-Eastman-Bechtel research team is studying the use of DME, instead of methanol, to generate formaldehyde, either externally or in situ. Methyl propionate (MP) is used as the propionyl source, instead of PA. The DME-based route can produce MMA in one step, and is possibly a cost-effective alternative to the methanol-based route.

RESULTS AND DISCUSSION

Task 1. Propionate Synthesis (Eastman and Bechtel)

Eastman has completed the experimental work and economic analysis for the overall process, and have completed their responsibilities per the statement of work for the original contract.

Task 2. Condensation Catalysis (RTI)

Over the last quarter (April-June, 1998), RTI's focus is to determine the long term stability of 10% Nb₂O₅/SiO₂ for condensation of propionic acid with formaldehyde with continuous activity/regeneration cycles. The goal is to study the effect of idle stage with N₂ purge on the stability and the regeneration efficiency.

In April, we have continued with follow-on characterization work on a 10-percent Nb/Si condensation catalyst, which was subjected to a long-term reaction-regeneration cycle study. In particular, RTI is analyzing the deactivated catalyst by BET-N₂ surface area, pore volume, XPS/ESCA, XRD, and ICP-MS to evaluate the causes of catalyst deactivation. The XPS/ESCA studies will be carried out at Eastman, and will measure the reduction in crystallite size of niobium, as a result of multiple reaction-regeneration cycles.

RTI has completed the BET-N₂ surface area and pore volume analysis, and has also completed the ICP-MS analysis. The ICP-MS analysis shows that there is no change in the bulk concentration of niobium in the fresh and deactivated catalyst, as shown in Table 1. The ICP-MS results also show that there is some residual F in the fresh catalyst batch, which results from the NbF₅ used as a precursor.

Table 1. ICP-MS Results on 10% Nb₂O₅/SiO₂ Catalyst

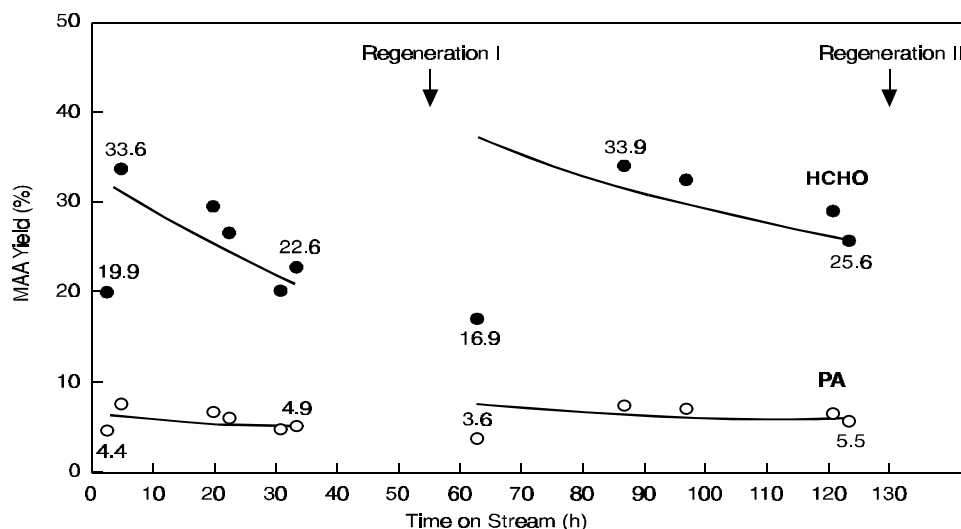
Catalyst	Nb (%)	Si (%)	F (%)
Fresh	12.3 ± 0.6	34.03 ± 0.6	1.03 ± 0.01
Deactivated	11.3 ± 0.5	37.1 ± 1.9	0.05 ± 0.00

The method used for ICP-MS analysis was described in the monthly report of April 1998.

Other accomplishments during the month of April include submission of a patent application entitled "Process for the Generation of α -, β -Unsaturated Acids and Esters using Niobium Catalysts", to the U.S. Patents and Trademarks Office.

In May, RTI had carried out another continuous condensation of formaldehyde with propionic acid over 10% Nb₂O₅/SiO₂ at 338°C. The results are summarized in Figure 2. During the first activity test period, the initial activity started low with 19.9% yield of MAA. However, the

following yield was quite high with 33.6%. Then, the activity slowly decreased to 22.6% after 33 hours on stream. The first regeneration was started after 55 hours on stream with about 100 cc/min of 2% O₂ in nitrogen at 400°C. O₂, CO₂ and CO emissions were monitored every 10 minutes during the first 2 hours. During the 2-hour period, the CO₂ concentrations were close to 2% and O₂ and CO concentrations were negligible which indicated that O₂ is completely consumed for combustion to CO₂. We therefore decided to let the regeneration continue through overnight. After 18 hours of regeneration, the emission of O₂, CO₂, CO was then taken again. The results with 2% O₂ and negligible CO₂ and CO indicated the regeneration was complete. The condensation reaction was then put on line for the second cycle. Again, the initial activity was low with 16.9% yield of MAA, but the following yield jumps to 33.9%. The activity then slowly decreased to 25.6% after 68.5 hours on stream.



Long-term continuous activity test on a 10% Nb₂O₅/SiO₂ catalyst
(Experimental conditions: T = 300 °C, 5 g (16-30) mesh catalyst, 72:16:220 mmol/h PA:HCHO:N₂)

Figure 2. Reaction-Regeneration Cycle Study on a 10%Nb₂O₅/SiO₂ catalyst.

The results indicate that 10% Nb₂O₅/SiO₂ deactivates slowly with time but can be regenerated to 100% of its original activity with similar stability using 2% O₂ in nitrogen at 400°C. However, after the second regeneration, the reaction was terminated because the material balance of the reaction is not acceptable and results are not reported. The used catalysts will be analyzed with BET, penetrometer, ICP-MS to determine the effect of deactivation and regeneration on catalyst properties. RTI will start another long term test after synthesize another batch of 10% Nb₂O₅/SiO₂ catalysts.

In June, RTI had reconstructed the reactor system including a new preheater and new temperature setting for the preheater. Glass preheater loaded with glass beads is heated with heating tapes to ~490°F(254°C, T1). The reactor inlet temperature with glass beads as another preheating zone is around 570°F(299°C, T2). And, the outlet temperature is ~480°F(249°C, T3). When the feed was added to the reactor system T1 temperature decreased because heat is required to crack trioxane to formaldehyde and for the vaporization of propionic acid. T2 and T3, on the other hand, decreased to 530°F(277°C) and increased to 525°F(274°C), respectively.

Continuous condensation of formaldehyde with propionic acid with regeneration are carried out over newly synthesized 10% Nb₂O₅/SiO₂. Five activity and four regeneration cycles have been completed so far. The results are summarized in Figure 3. During the first two activity cycles, only one yield result of each activity cycle is reported because the sample injection technique is

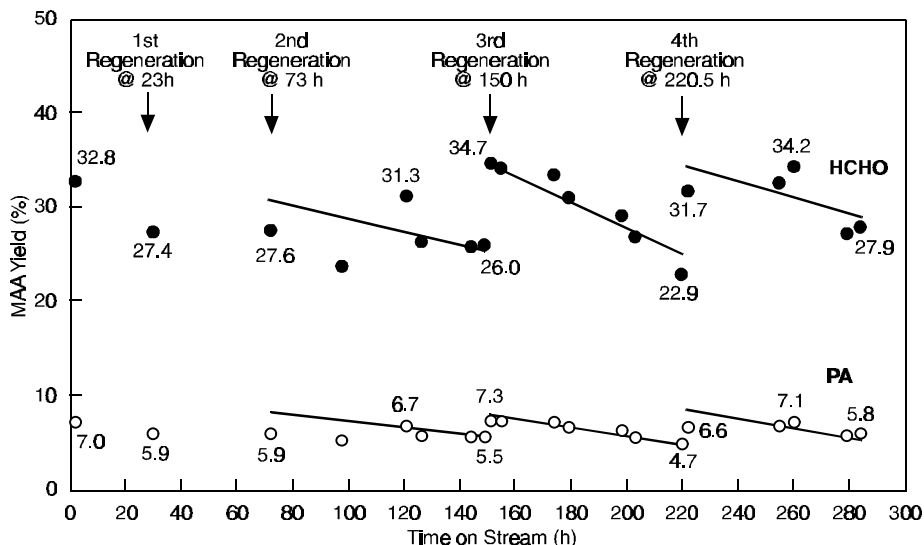


Figure 3. Extended long term reaction-regeneration cycle study on a 10%Nb₂O₅/SiO₂ catalyst.

not adequate and the syringe did not function properly. Starting from the third activity cycle the product analyses are taken and reported regularly. The results show that 10% Nb₂O₅/SiO₂ deactivates slowly with time but can be regenerated to 100% of its original activity with 2% O₂ in nitrogen at 400°C. For example, the fourth activity cycle decreases from the initial activity of 34.7% yield down to 22.9% yield of MAA over 70 hours. The activity was then regenerated to the original activity after the 2% O₂/N₂ regeneration. The activity/regeneration cycles continue with consistent 90-95% of carbon balance. The reaction is scheduled to complete with 6 activity cycles and 5 regenerations.

The used catalysts will be analyzed with TGA and XPS to determine bulk and surface coke content and coke properties. RTI will start the investigation of effects of propionic acid/formaldehyde ratio on reaction activity and product selectivity over 20% Nb₂O₅/SiO₂ catalysts.

Task 3. Slurry Reactor Studies (RTI and Eastman)

Based on Eastman's economic analysis, the RTI three-step route to MMA, based on a vapor phase condensation reactor, appears commercially promising. The slurry reactor technology will therefore be revisited at the end of the DME extension of this contract.

Task 4. DME Cost Estimation Study(Bechtel and Eastman)

Bechtel and Eastman will start the tradeoff analysis and preliminary plant/economics studies after RTI obtain the preliminary results of DME partial oxidation and methyl propionate condensation with formaldehyde.

Task 5. DME Condensation Study(RTI and Eastman)

RTI has developed a safety protocol for DME partial oxidation studies. Development of the analytical system for DME partial oxidation will soon be followed. RTI has also initiated the research on the condensation of methyl propionate with formaldehyde and completed the design of a fixed-bed microreactor system. RTI will synthesize catalysts for methyl propionate condensation reactions.

CONCLUSIONS

1. Status

Task 1 is complete and Task 2 should be completed after the completion of the long term test(6 activity cycles and 5 regenerations) and catalyst characterization. Current results indicate that 10%Nb₂O₅/SiO₂ can continuously condensate formaldehyde with propionic acid with slow deactivation. But, the activity can be regenerated to 100% of its original activity and selectivity. However, we have decided to test the effect of PA/HCHO ratio on reaction activity and selectivity over 20%Nb₂O₅/SiO₂. An new batch of 20%Nb₂O₅/SiO₂ will be synthesized for the condensation of formaldehyde with propionic acid with four PA/HCHO ratios. Task 3 is on hold and will likely be revisited during the DME extension or upon its completion. In Tasks 4&5 currently under way, RTI has designed, assembled, and operated a fixed-bed microreactor system for DME partial oxidation reactions. RTI has also continued to develop new catalysts for DME partial oxidation reactions and DME-MP condensation reactions.

The follow-on proposal prepared by RTI with support from Eastman and Bechtel is submitted to DOE in June. These follow-on studies will focus on evaluation of intrinsic kinetics and catalyst deactivation for formaldehyde condensation reactions, for the RTI three-step methanol route to MMA. The overall objective for this added work is to develop comparative economic packages for methanol and DME routes to MMA, so as to develop a cost-effective, environmentally benign, syngas-based route to MMA.

2. Forecast

RTI will continue to carry out follow-on work focused on characterization(TGA and XPS) of the used 10% Nb/Si catalyst, from the reaction-regeneration cycle study, to elucidate the causes for catalyst deactivation.

Current research on Task 5 (DME Condensation Studies) will focus on condensation reaction of methyl propionate with externally generated formaldehyde(trioxane), to evaluate different catalyst systems for the reaction. We feel that we should study the condensation between formaldehyde

with methyl propionate first before studying the DME partial oxidation because current condensation reaction system is ready and running and no other modification is needed. We will first evaluate the condensation of formaldehyde(trioxane) with methyl propionate over various supported niobium catalysts.

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