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# 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 (July-September, 1998), the project team has completed the continuous condensation of formaldehyde with propionic acid over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> at 300°C. Six activity and five regeneration cycles have been completed. The results show that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> deactivates slowly with time but can be regenerated to its original activity with 2% O<sub>2</sub> in nitrogen over night at 400°C. We have investigated the effects of regeneration, propionic acid/formaldehyde ratio (PA/HCHO=4.5/1 to 1.5/1) and reaction temperature (280-300°C) on reaction activity and product selectivity over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The regeneration effect on 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is similar to the effect on 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>. The regeneration can bring the deactivated catalyst to its original activity. However, the selectivity to MAA decreases with regeneration while the selectivity to DEK and CO<sub>2</sub> increases. When PA/HCHO ratio is decreased from 4.5/1 to 2.25/1 then to 1.5/1 at 300°C the MAA yield decreases but the MAA selectivity first increases then decreases. Decreasing the reaction temperature from 300°C to 280°C decreases the MAA yield from 39.5% to 30.7% but increases the MAA selectivity from 73.7% to 82.2%. The results indicate that both temperature and PA/HCHO ratio are important parameters to optimize the economic of the condensation between propionic acid and formaldehyde.

We have also investigated the condensation between methyl propionate and formaldehyde (MP/HCHO=4.5/1) at various reaction temperature (300-360°C) over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The conversions of HCHO and MP increase with reaction temperature. MMA+MAA selectivity goes through a maximum with the temperature. The selectivity to MMA+MAA is 72.3% at 320°C based on HCHO consumed. However, the activity and selectivity decreases rapidly with time on stream. The results suggest that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is an active catalyst for condensation of MP with HCHO, but deactivation needs to be minimized for the consideration of commercial application. We have also re-evaluated the analytical system for liquid product analysis. We conclude that FID is more accurate than TCD for large organic molecules analysis such as MMA, MAA, PA, DEK, and trioxane. However, TCD is necessary for HCHO, H<sub>2</sub>O, methanol, and MP analysis.

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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 (July-September, 1998), the project team has completed the continuous condensation of formaldehyde with propionic acid over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> at 300°C. Six activity and five regeneration cycles have been completed. The results show that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> deactivates slowly with time but can be regenerated to its original activity with 2% O<sub>2</sub> in nitrogen over night at 400°C. We have investigated the effects of regeneration, propionic acid/formaldehyde ratio (PA/HCHO=4.5/1 to 1.5/1) and reaction temperature (280-300°C) on reaction activity and product selectivity over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The regeneration effect on 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is similar to the effect on 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>. The regeneration can bring the deactivated catalyst to its original activity. However, the selectivity to MAA decreases with regeneration while the selectivity to DEK and CO<sub>2</sub> increases. When PA/HCHO ratio is decreased from 4.5/1 to 2.25/1 then to 1.5/1 at 300°C the MAA yield decreases but the MAA selectivity first increases then decreases. Decreasing the reaction temperature from 300°C to 280°C decreases the MAA yield from 39.5% to 30.7% but increases the MAA selectivity from 73.7% to 82.2%. The results indicate that both temperature and PA/HCHO ratio are important parameters to optimize the economic of the condensation between propionic acid and formaldehyde.

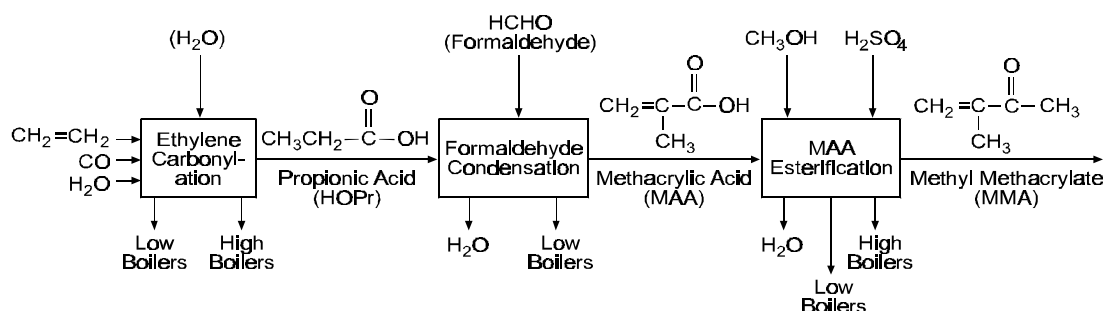
We have also investigated the condensation between methyl propionate and formaldehyde (MP/HCHO=4.5/1) at various reaction temperature (300-360°C) over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The conversions of HCHO and MP increase with reaction temperature. MMA+MAA selectivity goes through a maximum with the temperature. The selectivity to MMA+MAA is 72.3% at 320°C based on HCHO consumed. However, the activity and selectivity decreases rapidly with time on stream. The results suggest that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is an active catalyst for condensation of MP with HCHO, but deactivation needs to be minimized for the consideration of commercial application. We have also re-evaluated the analytical system for liquid product analysis. We conclude that FID is more accurate than TCD for large organic molecules analysis such as MMA, MAA, PA, DEK, and trioxane. However, TCD is necessary for HCHO, H<sub>2</sub>O, methanol, and MP analysis.



## 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 is now called as Task 4 and Task 5, and termed as DME Cost Estimation Study and DME Condensation Study, respectively.

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, RTI has completed the long-term continuous condensation of formaldehyde with propionic acid with regeneration over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> at 300°C. Six activity and five regeneration cycles have been completed. The total time on stream, not including the time for regenerations, for the reaction is about 400 hours. The results are summarized in Figure 2. The results show that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> deactivates slowly with time but can be regenerated to its original activity with 2% O<sub>2</sub> in nitrogen over night 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. After the 4th regeneration, the activity was brought back to 31.7% yield of MAA followed by slow deactivation which resulted in 25.5% yield after about 80 hours. The 5th regeneration resulted in similar regeneration and deactivation trend. The activity/regeneration cycles continue with consistent above 90% of carbon balance. Similarly, the PA yield follows the same deactivation and regeneration trend. Results suggest that silica supported niobium catalyst has the catalytic integrity (activity, selectivity and stability) for long term condensation reaction and the potential for commercial application for MAA and MMA manufacture.

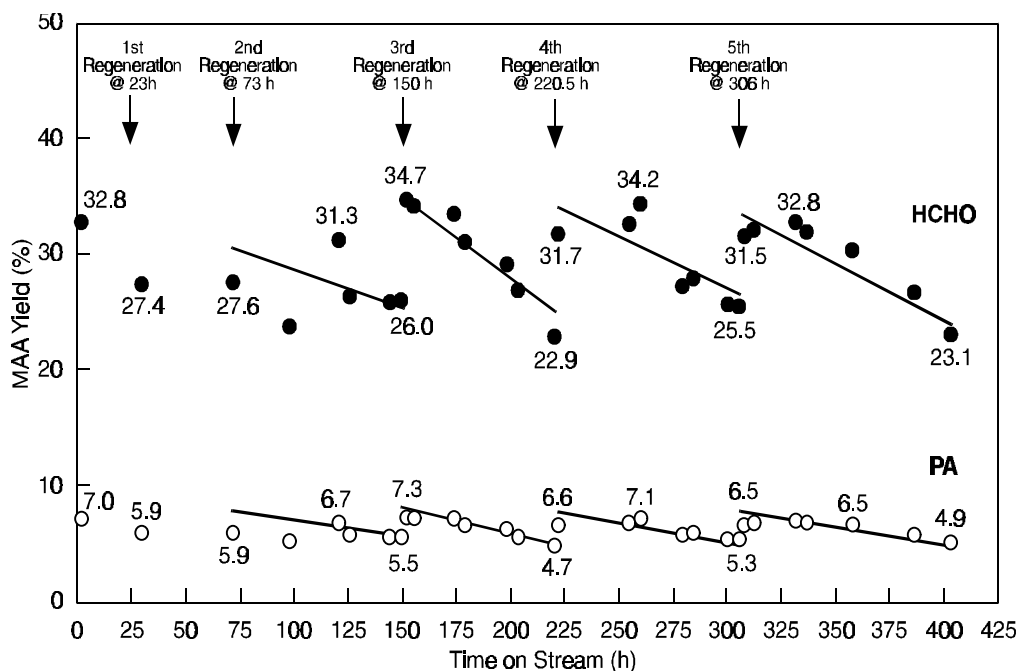


Figure 2. Long term reaction-regeneration cycle study on a 10%Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalyst.

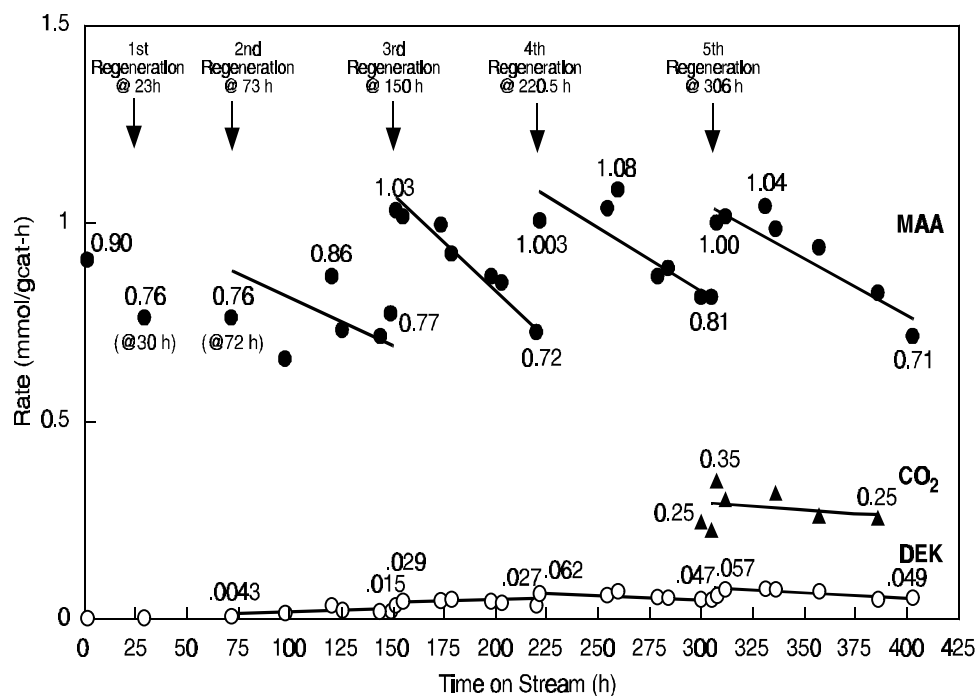


Figure 3. Rate formation of MAA, DEK, and CO<sub>2</sub> during the long-term run over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> at 300°C.

Rates of MAA (Based on HCHO), DEK, and CO<sub>2</sub> formation during the reaction are also summarized in Figure 3 to show the selectivity trends during the long term test. As shown in Figure 3, the rate to DEK is low compared with the rate of MAA formation and it stays pretty constant during each of the activity cycle. But, the rate increases with regeneration. For example, the rate of DEK formation is negligible during the 1st activity cycle, but it increases to about 0.057 mmol/g cat.-h after the 5th regeneration. Regeneration doesn't affect the formation rate of MAA but it increases the rate of DEK formation resulting in a decrease of the overall selectivity to MAA. We also measure the CO<sub>2</sub> formation rate by collecting the gaseous products with the Tedlar bag. Those include 2 data points at the end of the 5th activity cycle and 5 analyses for the 6th activity cycle. The results are included in Figure 3. The rate of CO<sub>2</sub> formation is relatively constant throughout the 6th activity cycle. It suggests that the decomposition activity of PA to CO<sub>2</sub> is not affected by the regeneration and catalytic deactivation.

We have also investigated the effects of regeneration, propionic acid/formaldehyde ratio (PA/HCHO=4.5/1 to 1.5/1) and reaction temperature (280-300°C) on reaction activity and product selectivity over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The regeneration effect on 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is similar to the effect on 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>. Results are summarized in Table I. The regeneration can bring the deactivated catalyst to its original activity. As shown in Table I, MAA yields are pretty constant with 39.9%, 36.8%, and 38.1% over fresh catalysts, catalysts after the first regeneration, and catalysts after the second regeneration, respectively. However, the selectivity to MAA decreases with regenerations from 84.% to 79.6% then to 74.0%. The selectivity to DEK, on the other hand, increases from 0.6% to 1.1% then 3.2% while CO<sub>2</sub> selectivity increases from 14.5% to 19.3% then to 22.8% with the regenerations. Regeneration, though reactivated the deactivated catalyst, has a detrimental effect on condensation selectivity.

Table I. Regeneration effect on MAA yield and product selectivity over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> at 300°C.

Catalysts	MAA Yield(%)	MAA Sel.(%)	DEK Sel.(%)	CO <sub>2</sub> Sel.(%)
Fresh	39.9	84.9	0.6	14.5
1 <sup>st</sup> regeneration	36.8	79.6	1.1	19.3
2 <sup>nd</sup> regeneration	38.1	74.0	3.2	22.8

The effect of PA/HCHO ratio is investigated from 4.5/1 to 1.5/1. When PA/HCHO ratio is decreased from 4.5/1 to 2.25/1 then to 1.5/1 at 300°C the MAA yield decreases from 39.5% to 31.8% then to 21.8% as shown in Table II. The lower resulted MAA yield is mainly contributed by the higher HCHO feeding rate to the reactor when decreasing the PA/HCHO ratio. The rate of MAA formation per unit time and per unit amount of catalysts actually increases with decreasing PA/HCHO ratio(i.e. increasing HCHO feeding rate). The results suggest that our first order assumption of MAA rate on HCHO is reasonable. The MAA selectivity first actually increases from 73.7% to 85.4% then decreases to 83.5% with decreasing PA/HCHO ratio. On the other hand, DEK by-product formation consistently decreases but CO<sub>2</sub> selectivity first decreases then increases with decreasing PA/HCHO ratio.

Table II. Effect of PA/HCHO ratio on MAA yield and product selectivity over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>.

Temp.(°C)	PA/HCHO	MAA yield(%)	MAA Sel.(%)	DEK Sel.(%)	CO <sub>2</sub> Sel.(%)
300	4.5/1	39.5	73.7	4.1	22.2
300	2.25/1	31.8	85.4	1.0	13.6
300	1.5/1	21.8	83.5	0.0	16.5
280	4.5/1	30.7	82.2	2.3	15.5
280	2.25/1	11.2	78.7	0.0	21.3

As shown in Table III, decreasing the reaction temperature from 300°C to 280°C decreases the MAA yield from 39.5% to 30.7% but increases the MAA selectivity from 73.7% to 82.2% when PA/HCHO=4.5/1. Both selectivities of DEK(4.1% to 2.3%) and CO<sub>2</sub>(22.2% to 15.5%) decrease when the temperature is decreased from 300°C to 280°C.

Table III. MAA yield and product selectivity at various temperatures over 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>.

Temp.(°C)	MAA Yield(%)	MAA Sel.(%)	DEK Sel.(%)	CO <sub>2</sub> Sel.(%)
300	39.5	73.7	4.1	22.2
290	33.6	NA	NA	NA
280	30.7	82.2	2.3	15.5

The results indicate that both temperature and PA/HCHO ratio are important parameters to optimize the economic of the condensation between propionic acid and formaldehyde.

Solid materials beside liquid products are also collected when PA/HCHO ratio is 1.5/1 at 300°C and 2.25/1 at 280°C. The materials are analyzed to determine the composition. The carbon and hydrogen contents of unknown are listed in Table IV with the theoretical compositions of formaldehyde and methacrylic acid polymers. As shown in Table IV, the carbon and hydrogen contents of the unknown material are 39.07% and 7.11%, respectively. We were unable to completely dry the sample because it evaporated at 60°C under vacuum, but did dry it with flowing nitrogen at room temperature over night. It is expected that hydrogen content may be off because of the moisture in the sample. By comparing with carbon and hydrogen content of formaldehyde(C: 40.0%, H: 6.72%) and methacrylic acid(C:55.8%, H: 7.02%) polymers and the low boiling point we believe that the unknown solid material is formaldehyde polymer.

Table IV. Carbon and hydrogen content of unknown solid and HCHO polymer and polymethacrylate.

	C(wt%)	H(wt%)
Unknown	39.07	7.11
HCHO polymer	40.00	6.72
Polymethacrylate	55.8	7.02

### **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)**

The investigation of the condensation between methyl propionate(MP) and formaldehyde (MP/HCHO=4.5/1) was carried out at temperatures from 300 to 360°C over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The results are summarized in Table V. The carbon balance of those tests ranges from 80-85%. The conversions of HCHO and MP increase with reaction temperature. For HCHO, the conversion increases from 49.0% at 300°C to 94.9% at 360°C. For MP, the conversion increases from 24.9% to 39.6% at temperatures from 300°C to 360°C. MMA and MAA selectivities based on HCHO consumed are also reported. MMA selectivity first increases from 41.2% to 60.4%

Table V. MP-HCHO condensation over 10%Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>.

Temp(°C)	HCHO Conv.(%)	MP Conv.(%)	MMA Sel.(%)	MAA Sel.(%)	MMA+MAA Sel.(%)
300	49.0	24.9	41.2	9.6	50.8
320	58.5	NA	60.4	11.9	72.3
340	84.6	34.8	44.4	7.1	51.5
360	94.9	39.6	35.4	7.5	42.9

when temperature was increased from 300°C to 320°C. Further increasing of the temperature to 340°C and 360°C decreases the selectivity to 44.4% and 35.4%, respectively. The MAA selectivity pattern is similar to that of MMA increasing from 9.6% at 300°C to 11.9% at 320°C then decreasing to 7.1% and 7.5% at 340°C and 360°C, respectively. The selectivity to MMA+MAA goes through a maximum with the temperature--72.3% at 320°C based on HCHO consumed. The results indicate fresh 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is an active catalyst for condensation of MP with HCHO. However, the activity and selectivity decrease with time on stream.

The deactivation trends at each reaction temperature are summarized in Table VI. The activity of catalyst decreases quickly with reaction time on stream. For example, at 320°C, the HCHO conversion decreases from 58.5% after 2.5 h on stream to 50.0% after 5.5 hours. The MMA+MAA selectivity decreases from 72.3% to 46.2%. It suggests that fresh 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is active and selective, but deactivation needs to be minimized for commercial application consideration.

Table VI. Deactivation of 10%Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> for condensation of MP with formaldehyde at temperatures from 300°C to 360°C.

Temp(°C)	Time on Stream(h)	HCHO Conv.(%)	MP Conv.(%)	MMA+MAA Sel.(%)
300	2.5	49.5	24.9	50.8
300	4.5	34.5	22.6	50.4
320	2.5	58.5	NA	72.3
320	5.5	50.0	26.1	46.2
340	2.5	84.6	34.8	51.5
340	5.0	69.4	31.8	44.5
360	3.0	94.9	39.6	42.9
360	5.5	88.5	37.8	39.1

We have also re-evaluated the analytical system for liquid product analysis. Several solvents including toluene, methylene chloride and acetone beside isopropanol were tested to collect soluble and liquid products with combination of FID and TCD as detectors for analysis. We conclude that isopropanol is the most adequate solvent and FID is more accurate than TCD for large organic molecule analysis such as MMA, MAA, PA, DEK, and trioxane. However, TCD is necessary for HCHO, H<sub>2</sub>O, methanol, and MP analysis. Both the retention times of methanol and MP are too close to the retention time of isopropanol to have accurate quantitative measurements when using FID method.

RTI has developed a safety protocol for DME partial oxidation studies. Partial oxidation will soon be tested over supported niobium catalysts.

## CONCLUSIONS

### 1. Status

Task 1 is completed. For Task 2, we have completed the long term test (6 activity and 5 regeneration cycles), condensation of PA with HCHO, over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>. Results indicate that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> can be continuously condense formaldehyde with propionic acid with slow deactivation. But the activity can be regenerated to 100% of its original activity. 20% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is synthesized and is tested for the condensation of formaldehyde with propionic acid with three PA/HCHO ratios and three reaction temperatures. The results indicate that both temperature and PA/HCHO ratio are important parameters to optimize the economic of the condensation between propionic acid and formaldehyde. Task 3 is on hold and will likely be revisited after the completion of DME extension. In Tasks 4&5 currently under way, RTI has designed, assembled, and operated a fixed-bed microreactor system for condensation of formaldehyde with methyl propionate and DME partial oxidation reactions. The investigation of the condensation of methyl propionate with formaldehyde (MP/HCHO=4.5/1) was carried out at various reaction temperature (300-360°C) over 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts. The selectivity to MMA+MAA reaches 72.3% at 320°C based on HCHO consumed. However, the activity and selectivity decrease rapidly with time on stream. The results suggest that 10% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is an active catalyst for condensation of MP with HCHO, but deactivation needs to be minimized for commercial application consideration. We have also re-evaluated the analytical system for liquid product analysis. Combination of FID and TCD GC methods will be used for product analysis.

### 2. Forecast

We will start evaluating the partial oxidation of DME to formaldehyde. Since silica supported niobium catalyst is active for direct condensation of MP with formaldehyde we will also first test its activity for partial oxidation of DME. 0.1% DME, 0.1% O<sub>2</sub> and balance N<sub>2</sub> will be used to evaluate the partial oxidation activity. In situ partial oxidation and condensation will soon follow.

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