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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. The research team has completed the research on the three-step methanol-based route to MMA. Under an extension to the original contract, we are 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(Oct.-Dec./98), we have investigated the condensation between methyl propionate and formaldehyde (MP/HCHO=4.5/1) at various reaction temperatures(280-360°C) over 5%, 10%, and 20% Nb₂O₅/SiO₂ catalysts. The conversion of HCHO increases with reaction temperature and niobium loading. MMA+MAA selectivity goes through a maximum with the temperature over both 10% and 20% Nb₂O₅/SiO₂. The selectivities to MMA+MAA are 67.2%, 72.3% and 58.1% at 320°C over 5%, 10%, 20% Nb₂O₅/SiO₂, respectively. However, the conversion of formaldehyde decreases rapidly with time on stream. The results suggest that silica supported niobium catalysts are active and selective for condensation of MP with HCHO, but deactivation needs to be minimized for the consideration of commercial application.

We have preliminarily investigated the partial oxidation of dimethyl ether(DME) over 5% Nb₂O₅/SiO₂ catalyst. Reactant gas mixture of 0.1% DME, 0.1% O₂ and balance nitrogen is studied with temperature ranging from 200°C to 500°C. The conversion of DME first increases with temperature reaching an maximum at 400°C then decreases. The selectivity to HCHO also increases with reaction temperature first. But the selectivity to HCHO decreases at temperature above 350°C accompanied by the increasing selectivity to CO₂. The results suggest that silica supported niobium catalysts are active for partial oxidation of DME to HCHO. Best temperatures for partial oxidation are between 300 and 400°C.

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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

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. The research team has completed the research on the three-step methanol-based route to MMA. Under an extension to the original contract, we are 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(Oct.-Dec./98), we have investigated the condensation between methyl propionate and formaldehyde (MP/HCHO=4.5/1) at various reaction temperatures(280-360°C) over 5%, 10%, and 20% Nb₂O₅/SiO₂ catalysts. The conversion of HCHO increases with reaction temperature and niobium loading. MMA+MAA selectivity goes through a maximum with the temperature over both 10% and 20% Nb₂O₅/SiO₂. The selectivities to MMA+MAA are 67.2%, 72.3% and 58.1% at 320°C over 5%, 10%, 20% Nb₂O₅/SiO₂, respectively. However, the conversion of formaldehyde decreases rapidly with time on stream. The results suggest that silica supported niobium catalysts are active and selective for condensation of MP with HCHO, but deactivation needs to be minimized for the consideration of commercial application.

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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 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 and Bechtel have 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. PA-HCHO Condensation Catalysis (RTI)

RTI has completed the condensation study of propionic acid and formaldehyde over various supported vanadium, niobium and tantalum 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 after the partial oxidation of DME and in-situ condensation with methyl propionate.

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)

HCHO-MP Condensation

The investigation of the condensation between methyl propionate(MP) and formaldehyde (MP/HCHO=4.5/1) are carried out at temperatures from 280 to 360 °C over 5%, 10%, and 20% Nb₂O₅/SiO₂ catalysts. The results are summarized in Table I. The carbon balance of those tests ranges from 80-98%. The conversion of HCHO increases with reaction temperature over all three catalysts. It increases from 38.8% at 300 °C to 51.8% at 320 °C for 5% Nb₂O₅/SiO₂, from 49.0% at 300 °C to 94.9% at 360 °C for 10% Nb₂O₅/SiO₂, and 36.7% at 280 °C to 86.0% at 340 °C for 20% Nb₂O₅/SiO₂. The condensation activity also increases with niobium loading. For example, at 320 °C, the conversion of HCHO increases from 51.5% for 5% Nb₂O₅/SiO₂ to 58.5% and 71.2% for 10% and 20% Nb₂O₅/SiO₂, respectively.

MMA and MAA selectivities based on HCHO consumed are also reported in Table I. MMA selectivity increases from 47.7% to 54.7% from 300 °C to 320 °C over 5% Nb₂O₅/SiO₂. For 10% Nb₂O₅/SiO₂, the MMA selectivity first increases from 41.2% to 60.4% when temperature was

Table I. Summary of methyl propionate condensation with formaldehyde(trioxane) over 5%, 10%, and 20% Nb₂O₅/SiO₂. Feed makeup: MP:HCHO:N₂=72:16:220 mmol/h.

Catalyst	Temp(°C)	HCHO Conv.(%)	MMA Sel.(%)	MAA Sel.(%)	MMA+MAA Sel.(%)
5% Nb ₂ O ₅ /SiO ₂	300	38.8	47.7	13.4	61.1
	320	51.8	54.7	12.5	67.2
10% Nb ₂ O ₅ /SiO ₂	300	49.0	41.2	9.6	50.8
	320	58.5	60.4	11.9	72.3
	340	84.6	44.4	7.1	51.5
	360	94.9	35.4	7.5	42.9
20% Nb ₂ O ₅ /SiO ₂	280	36.7	34.2	2.9	37.1
	300	55.9	42.8	7.6	50.4
	320	71.2	50.7	7.4	58.1
	340	86.0	35.5	5.4	40.9

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 over 10% Nb₂O₅/SiO₂ 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 total selectivity to MMA+MAA goes through a maximum with the temperature--72.3% at 320°C based on HCHO consumed. When 20% Nb₂O₅/SiO₂ is used the maximum MMA+MAA selectivity can only reach 58.1% at 320°C. The results indicate fresh 10% Nb₂O₅/SiO₂ is more selective than either 5% or 20% Nb₂O₅/SiO₂ for condensation of MP with HCHO to MMA and MAA. However, the activity and selectivity decrease with time on stream.

The deactivation trends at each reaction temperature over 10% Nb₂O₅/SiO₂, as an example, are summarized in Table II. 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%. The deactivation is much faster than the deactivation of the same catalysts for PA-HCHO condensation. It suggests that the deactivation is not simply caused by the polymerization of HCHO. Although Nb₂O₅/SiO₂ catalysts are active and selective for direct condensation of MP with HCHO, the results suggest that the deactivation needs to be minimized for commercial application consideration. In fact, we have added 2% of O₂ in the reactant mixture to minimize the deactivation since used catalysts can be regenerated with 2%O₂/N₂. But, the results indicate that the addition of O₂ doesn't slow down the deactivation. Although coke deposition proceeds quickly resulting in the deactivation at reaction temperature, its removal requires higher temperatures.

Table II. Deactivation of 10%Nb₂O₅/SiO₂ 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
	4.5	34.5	22.6	50.4
320	2.5	58.5	NA	72.3
	5.5	50.0	26.1	46.2
340	2.5	84.6	34.8	51.5
	5.0	69.4	31.8	44.5
360	3.0	94.9	39.6	42.9
	5.5	88.5	37.8	39.1

DME Partial Oxidation

We have preliminarily investigated the partial oxidation of dimethyl ether(DME). 0.1% DME, 0.1% O₂ and balance nitrogen purchased from National Welders is used for DME partial oxidation study. Total flow of 100cc/min of reactant mixture is passed over 5 grams of 5% Nb₂O₅/SiO₂ catalysts with reaction temperature ranging from 200°C to 500°C. The products are collected with 15ml of isopropanol at -5°C and a Tedlar bag. Because the concentration of DME is low with 0.1%, the product collection periods were extended to 3 to 5 hours to collect detectable formaldehyde. Both liquid and gaseous products are analyzed with GC-FID and GC-TCD. The results are summarized in Table III.

Table III. Partial oxidation of dimethyl ether to formaldehyde.

	200°C	250°C	300°C	350°C	400°C	450°C	500°C
DME Conv.(%)	18.4	13.8	27.6	72.9	90.7	84.7	77.8
HCHO Sel.(%)	2.0	9.9	26.7	34.4	11.9	6.5	2.3

0.1% DME, 0.1% O₂, balance N₂,
100cc/min, 5 g 5% Nb₂O₅/SiO₂.

The conversion of DME first increases with temperature reaching an maximum of 90.7% at 400°C then decreases. The selectivity to HCHO also increases with reaction temperature first. The highest HCHO selectivity is 34.4% at 350°C. But the selectivity decreases at temperature above 350°C accompanied by the increasing selectivity to CO₂.

The first increase then decrease of DME conversion and HCHO selectivity is expected with increasing reaction temperatures. Because the oxidation of DME could be partial or complete as shown in equations (1) and (2).

The stoichiometric ratios of DME to oxygen is 1:1 and 1:3 for partial and complete oxidation, respectively. During our tests 1:1 ratio of DME to oxygen mixture was used. If only HCHO is formed during the reaction the conversion of DME can be complete. If only CO₂ is formed from the oxidation of DME, the maximum conversion of DME can only reach 33.3%. At lower temperatures, the partial oxidation is relatively more favorable than at higher temperatures. The conversion of DME increases with temperature and more oxygen is used for conversion of DME to HCHO. At high temperatures, however, more CO₂ is formed from the complete oxidation with decreasing HCHO selectivity. It requires 3 times of oxygen for DME complete oxidation as of partial oxidation and causes the oxygen deficiency condition and the decrease of DME conversion.

Because the amount of products collected is close to the analytical detection limit of our system the carbon balance of the test are not satisfactory ranging from 50-80%. We will purchase a higher DME concentration mixture and modify the analytical procedures for future partial oxidation tests. The modification should improve the carbon balance and the results will be more quantitatively meaningful. However, the results do suggest that silica supported niobium catalysts are active for partial oxidation of DME to HCHO. Best temperatures for partial oxidation are between 300 and 400°C.

A short paper submitted to the ACS National Meeting at Anaheim(march 1999) was accepted for oral presentation. The title is "Catalytic Synthesis of Methacrylates over Silica Supported Niobium Catalysts" and will appear in the ACS preprints. A copy is attached in Appendix A of Dec./1998 monthly report. RTI and Eastman met at Kingsport, TN for project discussion on Dec. 16th. RTI made a presentation summarizing the accomplishment on HCHO-propionic acid condensation, investigation results on HCHO-methyl propionate condensation, and the preliminary results on partial oxidation of DME. A copy of presentation is attached in Appendix B of Dec./1998 monthly report.

CONCLUSIONS

1. Status

Tasks 1&2 are completed. Task 3 is on hold and will likely be revisited after the completion of DME extension. In Tasks 4&5 currently under way, we have investigated the condensation between methyl propionate and formaldehyde (MP/HCHO=4.5/1) at various reaction temperature (300-360°C) over 5%, 10% and 20% Nb₂O₅/SiO₂ catalysts. 10% Nb₂O₅/SiO₂ is more selective for the condensation of methyl propionate with formaldehyde (MP/HCHO=4.5/1) to MMA and MAA than 20% Nb₂O₅/SiO₂ and 5% Nb₂O₅/SiO₂. The selectivity to MMA+MAA reaches 72.3% at 320°C over 10% Nb₂O₅/SiO₂. However, the activity and selectivity decrease rapidly with time on stream for all three catalysts. The addition of 2% does not slow down the deactivation. The results suggest that 10% Nb₂O₅/SiO₂ is an active catalyst for condensation of MP with HCHO, but deactivation needs to be minimized for commercial application consideration.

Preliminary investigation of the partial oxidation of dimethyl ether (DME) was carried out over 5% Nb₂O₅/SiO₂ catalyst. The conversion of DME first increases with temperature reaching a maximum at 400°C then decreases. The selectivity to HCHO also increases with reaction temperature first. But the selectivity decreases at temperature above 350°C accompanied by the increasing selectivity to CO₂. The results suggest that silica supported niobium catalysts are active for partial oxidation of DME to HCHO. Best temperatures for partial oxidation are between 300 and 400°C.

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2. Forecast

We will further evaluate the partial oxidation of DME to formaldehyde over silica supported niobium catalysts. 2.0% DME, 2.0% O₂ and balance N₂ will be used to evaluate the partial oxidation activity to obtain reasonable amount of HCHO within normal collection period. In situ partial oxidation and condensation will soon follow.

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