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CATALYSTS AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

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MASTER

CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

DOE CONTRACT NO. 90PC90045

TEXAS A&M RESEARCH FOUNDATION PROJECT NO. 6722

Annual Report

Report Period: 10/01/90 to 9/30/91

PROJECT OBJECTIVES

The objectives of this project are to develop a new catalyst, the kinetics for this catalyst, simulate the performance of fixed bed trickle flow reactors, slurry flow reactors, and fixed bed gas phase reactors for conversion of a hydrogen-lean synthesis gas to isobutylene.

JUSTIFICATION FOR THE PROJECT

Isobutylene is a key reactant in the synthesis of methyl tertiary butyl ether (MTBE) and of isooctanes. MTBE and isooctanes are high octane fuels used to blend with low octane gasolines to raise the octane number required for modern automobiles. The production of these two key octane boosters is limited by the supply of isobutylene. MTBE when used as an octane enhancer also decreases the amount of pollutants emitted from the exhaust of an automobile engine.

Hydrogen-rich synthesis gas has been converted to isobutylene using a zirconia based catalyst. However, the productivity and yields are low, and the ability of the catalyst to convert a hydrogen-lean synthesis gas to isobutylene with high productivity and yields, and without excessive deactivation is unknown.

PROPOSED PROCESS

A hydrogen-lean synthesis gas with a ratio of H_2/CO of 0.5 to 1.0 is produced from the gasification of coal, lignite, or a biomass. This hydrogen-lean synthesis gas could be processed in a "shift reactor" with steam to convert the hydrogen-lean synthesis gas to a hydrogen-rich synthesis gas. But, this processing step is inefficient and consumes considerable energy. If the hydrogen-lean synthesis gas could be converted directly to isobutylene, a significant increase in process efficiency will be the result. We envision a reactor system and catalyst that will selectively and efficiently convert hydrogen-lean synthesis gas to isobutylene. The catalyst, based on past work published in the literature, will most likely be zirconia or thoria based, and will contain components to promote the water-gas shift reaction and increase the selectivity of isobutylene.

GOALS FOR THE YEAR

The goals for this year were to recruit and organize the project team, complete the literature and patent searches, complete the management plan and other reporting requirements, complete the revision and upgrading of existing bench scale units for the project, and synthesize, characterize and evaluate the catalytic activity of zirconia prepared (1) by co-precipitation of zirconyl nitrate with ammonium hydroxide and (2) by preparing a hydrous zirconium oxide using the modified sol gel method developed at the Sandia National Laboratories followed by calcination. The same preparation procedure would be used to prepare supports for impregnation with thorium nitrate, a potassium salt and a sodium salt. The synthesis of new crystalline zirconates were to be attempted with the objective of producing new compositions of matter which might have higher activities and selectivities than zirconia. Substantial progress on reactor and kinetic models for slurry and trickle bed reactors was to be achieved.

SUMMARY OF ACCOMPLISHMENTS FOR THE YEAR

This section presents a summary of the accomplishments for the year. Details are given in the manuscript prepared for the DOE contractors meeting, Sept. 1991. This manuscript is included in this report in the appendix.

Recruitment of the Research Team

The research team was recruited and consists of Mr. Walter Postula, a Ph. D. student, Mr. Z. Feng, a Ph.D. student, Dr. C. Erkey, a Post-Doctoral Research Associate, Dr. C. V. Philip, an Associate Research Scientist and the two co-principal investigators, Professors R. G. Anthony and A. Akgerman. Mr. Postula received his B. S. degree in Chemical Engineering from Texas A&M University in May, 1990 and began graduate school in September, 1990. He passed the Departmental Qualifying Examination for admission to the Ph. D. program in January, 1991. Mr. Feng completed the requirements for the M.S. degree January, 1991. His thesis was supervised by Professor Anthony, and was on the use of hydrous titanium oxide, hydrous Ti-Si oxide, and hydrous zirconium oxide as supports for nickel, molybdenum, platinum, and palladium for the dehydrogenation and aromatization of propane. Mr. Feng passed the Qualifying Examination required by the Chemical Engineering Department for admission to the Ph. D. program in May, 1990. Dr. Erkey received the Ph.D. degree from Texas A&M University in 1989, and has been working with Dr. Akgerman on measurement of diffusivities in Fischer-Tropsch liquids. He also directed Professor Akgerman's group when Professor Akgerman was on Sabbatical in the Fall of '89. Dr. C. V. Philip, Associate Research Scientist, received his Ph. D. in Chemistry in 1972, and has been working with Professor Anthony on coal liquefaction and catalyst projects since 1976.

Literature Search

A patent and literature search was completed, and as of this writing no new articles have been found that were not included in the review of the state of the art published in the proposal. However, from this review we have determined a need to conduct baseline experiments with a zirconia catalyst prepared by precipitation of zirconyl nitrate using ammonium hydroxide and impregnated with sodium hydroxide. The procedures published by Maehashi et al. (1984), Maruya et al. (1988, 1989) Oneshi et al. (1988) will be used.

Table 1 illustrates a first step at organizing this information into a condensed summary. A senior undergraduate student, Mr. Mike Fuchi compiled this table for us. The table illustrates the limited amount of work which has been performed on isobutylene synthesis since the work of Pichler and Ziesecke (1949). No U.S. patents have been issued on isobutylene synthesis from synthesis gas in the last ten years. A close examination of Table 1 shows that in recent years high selectivities of isobutylene from synthesis gas have been obtained at low pressures and at pressures up to 21 atmospheres when using zirconium dioxide as the catalyst. The production rate of isobutylene at 21 atmospheres is 1000 times the production rate at 0.2 atmospheres. There appears to be some loss in selectivity to isobutylene at the higher pressure. Isobutylene production rates at 50 atmospheres should be even greater than those at 21 atmospheres.

The mechanism for isobutylene synthesis is unknown, but the active sites appears to be different from the sites for producing alcohols and linear hydrocarbons. Maruya et al. (1989) report the following postulates: (1) methanol may be formed from a methoxy species, (2) there is no evidence for decomposition of CO to C(s) and O(s), (3) formaldehyde is formed with no induction time, (4) hydrocarbons are formed with no induction time, (5) $CH_xO_y(s)$ is a possible intermediate in hydrocarbon formation, and (6) they present data to eliminate formation of hydrocarbons by aldol condensation.

Reporting Requirements

All of the reports, management plan, monthlies, cost plan and status and quarterlies have been filed.

Bench Scale Reactor Systems

Two bench scale rector systems are being used in the project. The first one was an existing unit, which has been modified to conduct catalytic activity tests. A new gc and a Carle refinery gc were installed on-line. With this unit on-line analysis of the total reactor effluent can be achieved. This unit is referred to as BR#1. The second unit is a CDS 900 reactor system manufactured by Chemical Data Systems. (Chemical Data Systems was purchased from Autoclave Engineers in 1990, and the unit is call AE BTRS 900 by Autoclave Engineers. We will continue to use the designation CDS 900.) The unit uses a tubular reactor with controls and on-line analysis of the reactor products. All products in the reactor effluent are analyzed on-line, but 1-butene and isobutene elute simultaneously. Therefore, an off-line analysis is conducted to determine the ratio of 1-butene to isobutene. The composition of isobutylene and 1-butene are then calculated from this additional information.

Catalysts Synthesis and Characterization

Several batches of zirconia were prepared by precipitation of zirconyl nitrate with ammonium hydroxide at different pH for the precipitation. The active catalysts were prepared by calcining at 500 °C for 4 hours. The catalysts evaluated were predominately monoclinic zirconia, and the activity test were conducted in BR#1 prior to installation of the Carle Refinery gc for hydrocarbon, CO, CO_2 and H_2 on-line analysis. Therefore, all of the analysis were conducted off-line for this series of experiments. The results obtained with this unit compared favorably with data reported by UOP for a zirconia prepared by co-precipitation of zirconium chloride with ammonium hydroxide. The catalysts were referred to as C1.

A zirconia was prepared from hydrous zirconium oxide by calcination at 600 °C. The activity and product distributions for this catalysts were different than those obtained for catalysts C1. The results of these experiments are reported in the manuscript submitted to the DOE

Contractors meeting, September 1991.

A new zirconate was synthesized with a first reflection of the XRD pattern at 1.2 nm. This material appears to be a new composition of matter, because no Raman spectra or XRD patterns have been found in the literature, patent literature, or data bases, which match the spectra and pattern obtained for the new material. Activity testing is planned for the coming year.

Kinetic and Reactor Modelling

Two approaches are being used for developing kinetic models for these reactions. The first is the classical approach of using macrokinetic models and the second is the use of microkinetic models. For the first approach experimental data from activity testing and kinetic experiments are used. For the second approach, a detailed kinetic mechanism composed of many elementary steps is used. Published adsorption data and theoretical calculations are used to obtained the first approximation of the specific rates of the individual reactions. Judiciously planned experiments are then used to refine the model. The latter approach should increase our understanding of the probable mechanisms occurring in the selective synthesis of isobutylene, and lead to a macrokinetic model. This macrokinetic model should incorporate more detail and could be a better predictor of the reactor and catalyst performance than a macrokinetic model developed by the first approach which is all empirical.

Development of the programs for modelling the trickle bed reactors is proceeding in a satisfactory manner. Preliminary results on the modelling effort are presented in the Appendix.

GOALS FOR THE SECOND YEAR

The goals for the coming year are to continue the synthesis, characterization and evaluation of catalytic activity for new catalyst preparations, file necessary reports, continue and essentially complete the kinetic model, and essential complete the programs for the trickle bed and slurry reactors. For the fixed bed gas phase reactors plug flow is being assumed and SimuSolve is being used for model development and parameter estimation.

During the first quarter of the second year the following activities are planned.

1. Prepare a zirconia from $K_{0.3}ZrO$ which is to be synthesized using procedure developed by R. G. Dosch at the Sandia Laboratories. Make at least 50 grams. Take the potassium zirconium oxide and ion exchange with HCl at a pH of 3. Do at least three

exchanges with filtering and washing (after an acetone rinse pull air through the filter 5 minutes before reslurring in water) between each exchange. Then take 20 grams and ion exchange with ammonium hydroxide at pH of 10 three times with filtering and air drying (5 min.) in between. Do not use water in any of the rinses, use acetone only. After the final ammonium hydroxide exchange, i.e. the pH stays at 10 for 10 minutes on re slurring, calcine at 600 °C for 4 hours. This is the catalyst to be placed into the reactor. XRD and surface areas need to be determined on a sample after calcination and after reaction. A potassium analysis using the AA is also needed. TGA and DTA analysis on catalysts samples used before and after reaction are also to be conducted.

Take the other 20 grams and adjust the potassium level to a pH of 0.4 wt% by ion exchange. Calcine for 4 h at 600 °C, etc.. Do all rinses with acetone. Final pH prior to calcination should be about 10. Addition of ammonium hydroxide may be required to maintain a pH of 10.

Activity testing: Do the test at a temperature, pressure and residence time (space velocity) to obtain 20% conversion of CO. This will be the base case. Then do a matrix of residence time 50% less and 50% greater, and temperatures 25 ° higher and 25 °C lower than the base case.

Kinetics: Use Simusolve to obtain a rate equation for CO disappearance, hydrogen disappearance and $CO+H_2$ disappearance. This needs to be done for the experiments conducted in August.

2. Obtain data on zirconia at low temperatures for the purposed of producing methanol. Kinetic data in the low temperature region are needed by Dr. Can Erkey for the microkinetic model development. Three or four space velocities and three temperatures are to be used. The three temperatures will be done only at the base case velocity.

3. Prepare the ppt. zirconia. In the hydrous form add sodium hydroxide to obtain 0.1, 0.3 and 0.5 wt% sodium. Final pH should be about 10. Calcine at 600 °C.

   Activity testing: see above comments.

   Kinetics: See above.

4. Dr. Philip has prepared a zirconia catalyst impregnated with thorium nitrate and then calcined. This catalyst will be evaluated in the CDS 900 unit.

5. Reproduce the synthesis of the 1.2 nm d_0 spacing zirconate, and prepare at least a 100 g batch of the same.
6. Take 20 g and remove the sodium by ion exchange with HCl to a level of less than 0.5 wt%. Then adjust the pH to 10 with ammonium hydroxide. Three NH_4OH treatments may be required. See above comments. Calcine at 600 °C for 4 hours and then get surface areas, AA, and XRD analysis. The sample which is prepared will be used for catalytic activity testing.
7. Continue the development of the microkinetic model.
8. Other experiments will be planned based on the results of the experiments conducted above and the model development.