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# CATALYST AND PROCESS DEVELOPMENT FOR SYNTHESIS GAS CONVERSION TO ISOBUTYLENE

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# EXTENDED ABSTRACT

This project was initiated because the supply of isobutylene had been identified as a limitation on the production of methyl-t-butyl ether, a gasoline additive. Prior research on isobutylene synthesis had been at low conversions (less than 5%) or extremely high pressures (greater than 300 bars). The purpose of this research was to optimize the synthesis of a zirconia based catalyst, determine process conditions for producing isobutylene at pressures less than 100 bars, develop kinetic and reactor models, and simulate the performance of fixed bed, trickle bed and slurry flow reactors.

Results and accomplishments of this project are as follows:

- Thermodynamic and kinetic constraints for producing isobutylene at high yields were identified. In the ultimate thermodynamic limit, methane, carbon, carbon dioxide and water are the major equilibrium products at CO conversions of $99^+$%. For $C_2$ through $C_6$ olefins the $C_5$ olefins are the thermodynamically favored comprising 50.1% of the product. The $C_4$ olefins comprise only 24.5 % of the product with isobutylene being only 46% of the $C_4$s. Production of alkanes is thermodynamically more favorable than the olefins. Even though these are thermodynamic compositions, the synthesis of isobutylene from synthesis gas is a series type of reaction, therefore intermediate components can be produced with selectivities and product distributions substantially different from the distributions predicted from thermodynamics. However, a series reaction has kinetic limitations. At the most favorable conditions a significant part of the product will be components other than the desired component. The primary limit for synthesis of isobutylene from synthesis gas is a kinetic limit on the yield.

- Three types of zirconia based catalysts were prepared, which resulted in the production of isobutylene within the kinetic and thermodynamic constraints of the system. All three catalysts resulted in the production of a $C_4$ distribution with $60^+$% isobutylene and one catalyst, prepared hydrothermally, produced a $C_4$ distribution of only isobutane and isobutylene. This catalyst while extremely active also produced a high yield of methane. A catalyst prepared by a modified sol gel technique also resulted in production of a $C_4$ distribution with predominantly isobutane and isobutylene. However, the third catalyst, which was prepared by precipitation and contained cerium, was the most active of the three catalyst. Isobutylene in the $C_4$ fraction was equal to or greater than 90%. Hydrocarbons, which were produced by using all of the catalysts, were predominantly olefins, and the $C_4$ hydrocarbons constituted 15 wt% to 34 wt% the product. These numbers are in the vicinity of the expected equilibrium $C_4$ olefin distribution. However, isobutylene content of the $C_4$ fraction was 60 to 90% of the $C_4$s, which is significantly greater than the equilibrium $C_4$ distribution. The major group of components was the $C_5+$, which was predominantly iso $C_5$ olefins. This group comprised from 30 to 70 wt% of the hydrocarbons produced. In many instances the $C_2$ through $C_6$ distribution had characteristics similar to the equilibrium distribution of the $C_2$ through $C_6$ olefins presented above, i.e the $C_4$ content was nearly always less than the $C_5$s. Therefore, depending on the economics and the desired product distribution, one of the three

catalysts could be utilized.

- Reaction temperatures of 400 °C or greater were required to minimize the production of oxygenates, which were composed mostly of dimethylether.

- The hydrothermally prepared catalyst resulted in the production of large amounts of methane, because of hydrocracking of the $C_5$+ fraction.

- Optimum carbon monoxide conversions for minimizing methane production and maximizing the $C_4$ fraction for all three catalyst were in the range of 10 to 15%. The temperatures were 400 to 450 °C and reactor pressures were 50 to 70 atmospheres. Space velocities for the conditions were in the range of 800 to 2000 $h^{-1}$.

- With extended time on stream and cycling of the temperatures up and down the production of methane increased. Co-feeding of hydrogen sulfide with CO and hydrogen seemed to moderate the effect of this ageing phenomena. Also, co-feeding of $H_2S$ resulted in a $C_5$ fraction, which was predominantly 3-methyl-1-butene. This olefin might be isomerized in a subsequent step to 2-methyl-2-(or 1) butene for production of tertamylmethylether (TAME). Coking on the catalyst did not result in any significant deactivation.

- Oxygen vacancies are required for an active catalyst and may be responsible for the unique selectivity of isosynthesis catalysts. A catalyst doped with 1.72% Mg (wt) was the most active singly-doped zirconia with a CO conversion of 29% (32 wt% $C_1$, 29 wt% $C_4$, 26 wt% $C_5$+) at 673 K, 50 atm, 1/1 $CO/H_2$ ratio, and 90 second space time. A dopant that introduced the most oxygen vacancies per cation and was close in size to zirconium gave a more active catalyst. A multicomponent doped (Y-Ba-Cu) zirconia was more active but produced more methane. Multiple dopings of zirconia may be the course needed to produce active catalysts at lower temperatures.

- An active isosynthesis catalyst requires approximately equal number of acidic and basic sites to be selective.

- Operation of slurry and trickle bed reactors illustrated the ability of utilizing these types of reactors for producing isobutylene from synthesis gas. The starting solvent used to co-feed with synthesis gas was decalin. However, as the operation continued the high boiling compounds produced in the isosynthesis comprised part of the liquid recycle. Hydrocracking of the high boiling components occurred resulting in an increase in the production of propylene from the process.

- Kinetic and reactor models were developed for the fixed bed gas phase, the trickle bed and the slurry reactors. Carbon dioxide was found to inhibit the rate of isosynthesis.

A catalyst, reactor models and optimum operating conditions have been developed for producing isobutylene from coal derived synthesis gas. The operating conditions are much less severe than the reaction conditions developed by the Germans during and prior to WWII. The low conversions, i.e. CO conversions less than 15%, have been perceived to be undesirable for a commercial process. However, the exothermic nature of the reaction and the ability to remove heat from the reactor could limit the extent of conversion for a fixed bed reactor. Long residence times for trickle or slurry (bubble column) reactors could result in high CO conversions at the expense of reduced selectivities to iso $C_4$ compounds. Economic studies based on a preliminary design, and a specific location will be required to determine the commercial feasibility of the process.

## OBJECTIVES OF THE RESEARCH

The objectives of this project are to develop a new zirconia-based catalyst; the kinetics of the reactions occurring over this catalyst; reactor models for trickle bed, slurry and fixed bed reactors; to and 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.

*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 biomass. This hydrogen-lean synthesis gas can be processed in a "shift reactor" with steam to convert the hydrogen-lean synthesis gas to a hydrogen-rich synthesis gas. However, this processing step is inefficient and consumes a considerable amount of 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-based, and will contain components to promote the water-gas shift reaction and increase the selectivity of isobutylene.

### *Report Format*

This report is divided into Introduction, Experimental, Catalysts Evaluation-Results and Discussion, Modelling-Results and Discussion, Conclusions and Recommendation sections. Space time is also used throughout the report. However, reciprocal space time multiplied by reaction pressure in atm, divided by reaction temperature in Kelvin and multiplied by 982,800 will give the space velocity in reciprocal hours valuated at 273 K and 1 atm. The Tables and Figures for each section follow the last page of text in that section. Appendix C contains a listing of publications and presentations based on this work.

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3.66 Predicted conversion over 7% Ce-$ZrO_2$ at 673 K, 50 atm, and 1/1 $CO/H_2$ ratio, with and without $CO_2$ inhibition

3.67 Changes in predicted conversion over 7% Ce-$ZrO_2$ at 673, 50 atm, and 1/1 $CO/H_2$ ratio with *n*

3.68 Predicted conversion over 7% Ce-$ZrO_2$ at 673 K, 50 atm, and 1/1 $CO/H_2$ ratio with CO inhibition

3.69 Comparison of experimental and predicted carbon monoxide conversion for all catalysts

## LIST OF FIGURES (Continued)

FIGURE

3.70 Determination of activation energy over 7% Ce-$ZrO_2$ (ppt.) with aluminum CO cylinder at 50 atm and 1/1 CO/($H_2$+$H_2S$) ratio

3.71 Determination of the heat of adsorption for $CO_2$ over 7% Ce-$ZrO_2$ (ppt.) with aluminum CO cylinder at 50 atm and 1/1 CO/($H_2$+$H_2S$) ratio

3.72 Comparison of experimental and predicted $C_1$-$C_5$+ production rates over 7% Ce-$ZrO_2$ at 673 K, 50 atm, and 1/1 CO/$H_2$ ratio

3.73 Product distribution generated by the semi-empirical model over K-$ZrO_2$ (MSG), at 723 K, 70 atm, 1/1 CO/$H_2$ ratio, and 80 second space time

3.74 Parameters in the semi-empirical model. The distribution in Figure 3.73 is plotted on a semi-log scale, and $\alpha$ and $\kappa$ are related to the slopes of the line segments

3.75 Production rates of $CH_4$ and $C_4$ hydrocarbons. Calculated by combining the semi-empirical model for hydrocarbon distribution with the empirical CO reaction rate. $ZrO_2$ (H-0304), 723 K, 70 atm, and 1/1 CO/$H_2$ ratio

3.76 Residual plots for hydrocarbon distributions. For all the catalysts in Table 3.30 at 723 K, 70 atm, and 20 to 80 second space times