

HYDROCARBON SYNTHESIS FROM DIMETHYL ETHER OVER ZSM-5 CATALYST

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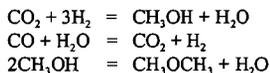
ABSTRACT

The liquid phase synthesis of dimethyl ether from syngas has significant advantages over the liquid phase methanol synthesis in the areas of syngas conversion and reactor productivity. The merits of this dual catalytic process allows dimethyl ether to be utilized as a viable feedstock for petrochemical synthesis. In particular, dimethyl ether can be converted to hydrocarbons using H-ZSM-5 type zeolite catalysts. Appropriate choice of the acidity of the zeolite catalyst as well as the operating parameters such as reaction temperature, partial pressure and space velocity of dimethyl ether dictate the product spectrum, ranging from lower olefins (ethylene and propylene) to gasoline-range hydrocarbons. The focus of this paper is to thoroughly study the aforementioned details of this process and compare its merits with methanol conversion.

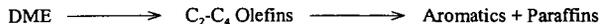
INTRODUCTION

The synthesis of petrochemicals from syngas via methanol has been the focus of research in the chemical industry for several decades. Methanol synthesis from syngas is a well established technology (Lee, 1990). However, the methanol synthesis technology faces a serious impediment because the reaction is severely limited by chemical equilibrium. Due to the reversible nature of the methanol synthesis reaction, the maximum per-pass conversion of syngas is restricted. However, the potential of the reverse reaction and the chemical equilibrium limitation can be alleviated by chemically converting methanol into another chemical species that is not affected by the equilibrium constraint. The in-situ dehydration of methanol to dimethyl ether (DME) is based on this approach.

Of particular interest is the novel process that has been developed by Lee and his co-workers for the co-production of dimethyl ether and methanol from syngas (Lee, 1992). This liquid phase dimethyl ether (LPDME) process consists of a dual-catalytic synthesis in a single reactor stage. Methanol is synthesized over coprecipitated Cu/ZnO/Al₂O₃ catalyst, whereas dimethyl ether synthesis takes place over γ -alumina catalyst. The reactions take place in a liquid phase system involving inert hydrocarbon oil such as Witco-40, Witco-70, Frecczene-100, etc. Various aspects of the methanol synthesis reaction and the co-production of dimethyl ether reaction have been assessed for commercialization of the process (Gogate, 1992). The process merits such as reactor productivities, catalyst life and activity, etc. were significantly higher in the co-production case. For high productivity cases using very high weight hourly space velocities of syngas, the single-stage productivity can be increased by as much as 70%. In terms of catalyst deactivation, the rate of thermal aging of methanol synthesis catalyst becomes slower when it is used in a co-production mode along with γ -alumina. Moreover, the process exhibits excellent control because it is possible to co-produce dimethyl ether and methanol in any desired proportion, from 5% DME to 95% DME, by varying the mass ratios of the methanol synthesis catalyst to the methanol dehydration catalyst. From the economic point of view, dimethyl ether produced from syngas is substantially cheaper than methanol synthesis on a methyl productivity basis. This cost benefit and enhanced effectiveness provides an alternative route to produce a variety of petrochemicals from DME as a starting raw material. The process chemistry is as follows:



Synthesis of lower olefins from methanol over ZSM-5 catalyst has been investigated in detail (Chang, 1983). Lower olefins synthesis from methanol over smaller pore size ZSM-34 catalyst has also been studied (Givens, 1978). Selective conversion of dimethyl ether to lower olefins is a process of growing potential in the chemical industry. Lower olefins are intermediates in the conversion of dimethyl ether to hydrocarbons over ZSM-5 type zeolite catalysts. The reaction pathway can be represented as follows:



Of particular interest is the synthesis of ethylene and propylene from dimethyl ether because of their growing demand as raw materials for a number of petrochemicals. Besides chemicals like ethylene oxide, ethylene glycol, propylene oxide, etc. these olefins are the building blocks for the production of their respective polymers, polyethylene and polypropylene. These polymers are widely used in everyday life applications such as molded plastic items, plastic packaging films, etc. Increasing demand for isobutene is inevitable since isobutene is used as the raw material for MTBE (methyl tert-butyl ether), a high octane gasoline blending oxygenate. Isobutene is also used in the manufacture of methyl methacrylate and isoprene. 1-Butene and 2-Butenes are important ingredients in the synthesis of methyl ethyl ketone. Thus, lower olefins have varied usage in the chemical industry, and so the research devoted toward their production from non-petroleum sources is of economic interest.

EXPERIMENTAL

A schematic of the DME-to-hydrocarbons experimental system is shown in Figure 1. The system can be divided into several sections: feed gas blending section, reaction section, and product separation and analysis section. The feed gas section consists of three mass flow controllers for DME, nitrogen, and carbon dioxide, respectively. A fixed bed reactor 18" in length and 0.5" I.D., manufactured by Autoclave Engineers has been utilized for this study. An axial thermowell runs the entire length of the tube and allows for measurement of the temperature profile in the reactor. The reactor tube is completely filled with 1/16" inert ZrO₂ beads. These beads are highly thermally stable and facilitate heat transfer from the beaded heater to the catalyst. Use of the beads in the reaction zone also helps dilute the reaction exotherm and therefore helps maintain a uniform temperature profile.

The feed gas analysis (DME, nitrogen and in some cases, carbon dioxide and methanol) as well as the analysis of the hydrocarbon product (C₁-C₅ range) was carried out using gas chromatography. The gas samples were withdrawn from the system using a constant rate 50 µl Hamilton syringe, as well as gas sampling bags. The liquid hydrocarbon product (C₅⁺ paraffins and aromatics) was analyzed using gas chromatography/ mass spectrometry.

RESULTS AND DISCUSSION

The assessment of process feasibility of DME conversion to lower olefins, particularly ethylene and propylene, has been carried out over ZSM-5 type zeolite catalysts (Sardesai, 1997). The results obtained from this research have revealed important relevant information about this process. Over the conventional ZSM-5 catalyst (SiO₂/Al₂O₃ ratio of 150), lower olefin (C₂-C₄) selectivity of 70 wt.% of total hydrocarbons was achieved. One of the salient features of this process is that it can be customized to target an individual olefin in the C₂-C₄ range at the expense of the other lower olefins. Process parameters such as operating temperature, partial pressure of DME, contact time, and catalyst acidity were evaluated over a limited range in light of maximizing lower olefin selectivity at optimal conditions. The results indicated that the temperature of the reaction has to be kept high, the partial pressure of DME has to be kept low, and the contact time of the reactants with the catalyst has to be kept low as shown in Figures 2-4. The concentration of strong Bronsted acid sites on the ZSM-5 catalyst has to be kept low by maintaining a lower SiO₂/Al₂O₃ ratio as shown in Figure 5. Also, the pore size of the catalyst has to be small enough to control the product spectrum on the higher end, and has to be large enough not to be a target of rapid deactivation by coking. Optimum results for lower olefin synthesis were obtained using the following parameters: Temperature = 430C, vol% Nitrogen in Feed = 65%, weight hourly space velocity of DME = 30 h⁻¹, SiO₂/Al₂O₃ ratio of ZSM-5 catalyst = 150.

Methanol conversion to hydrocarbons can be represented as follows:



where [CH₂] is the average representation of the hydrocarbon product. The conversion is essentially complete and stoichiometric. The above reaction shows a 44% selectivity by weight toward hydrocarbons, and a 56% selectivity toward water.

Dimethyl ether conversion to hydrocarbons can be represented as follows:



where [CH₂, CH₂] is the average representation of the hydrocarbon product. The conversion is essentially complete and stoichiometric. The above reaction shows a 60.8% selectivity by weight toward hydrocarbons, and a 39.2% selectivity toward water. Thus at nominally identical conditions, the selectivity toward hydrocarbons is 38% higher in the dimethyl ether conversion case as compared to the methanol conversion process (Lee, 1996).

In the methanol to hydrocarbons process, methanol formed from syngas first dehydrates to dimethyl ether in the first, and then an equilibrium mixture of methanol, dimethyl ether, and water is converted in the second reactor to form hydrocarbons. The exothermic of reaction is -398 cal/g methanol converted. The

methanol dehydration step of the reaction liberates 15% of the reaction heat, whereas the rest is given off in the latter step. In the dimethyl ether to hydrocarbons process, the exothermic heat liberated is only 85% of that of the methanol conversion process. This is because dimethyl ether is produced in the syngas reactor, whereas, in the methanol case, dimethyl ether is produced in the dehydration reactor. Thus, the heat management is better in the dimethyl ether conversion process. In addition to this, it obviates the need of a dehydration reactor thereby causing considerable saving in capital investments and working capital.

Dimethyl ether can also be converted to gasoline-range hydrocarbons using ZSM-5 catalysts of very high acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30). The experimental and testing results have been very promising from a commercial standpoint. A U.S. patent for the process has been issued (Lee, 1995).

CONCLUSIONS

As a long term commodity chemical, dimethyl ether is proving to be one of the chemical industry's most dynamic product. It can be produced from any fossil fuel source. It finds use as an alternate fuel, as well as a chemical feedstock. Technical and market application efforts are proceeding at a great pace on both its production and uses on an international basis. Dimethyl ether can be easily converted to ethylene and propylene, the building blocks of the chemical industry, using this process which has distinct advantages over methanol conversion. Thus, natural gas-based syngas can be converted to hydrocarbons via dimethyl ether as an intermediate using zeolite catalysts. The merits of this process are very attractive and have been investigated in detail for pre-scale up assessment. The demonstrated process feasibility and excellence are novel and very promising in developing alternative sources for lower olefins.

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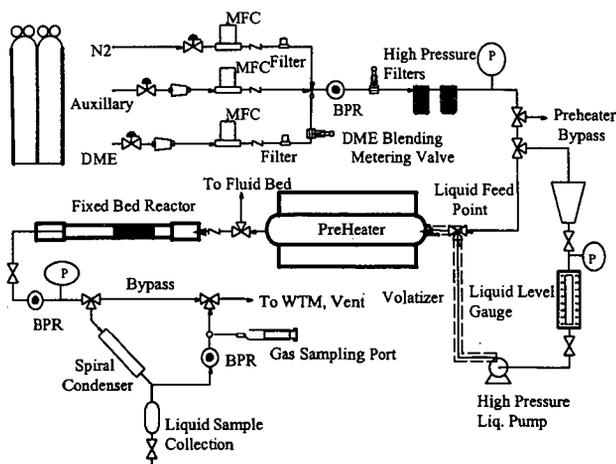


Figure 1. Schematic of the Dimethyl Ether (DME) to Hydrocarbons Experimental Unit.

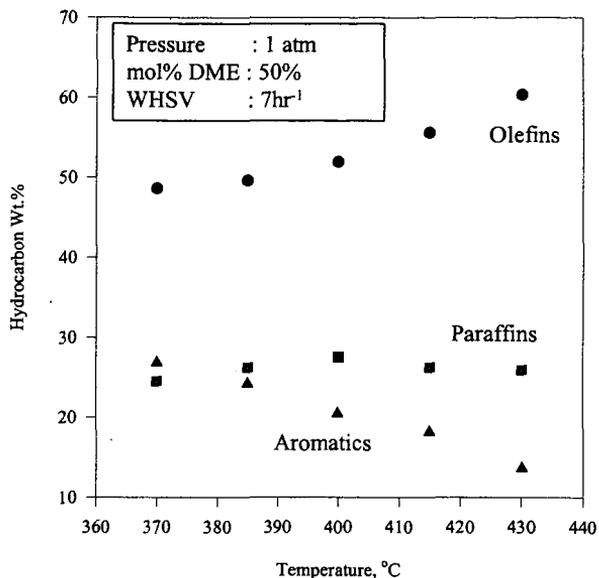


Figure 2. Effect of Reaction Temperature on Hydrocarbon Selectivity

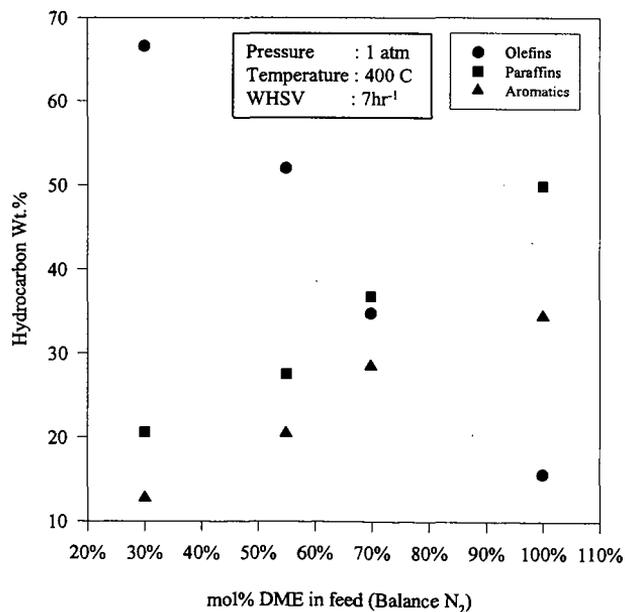


Figure 3. Effect of Feed Dilution on Hydrocarbon Selectivity

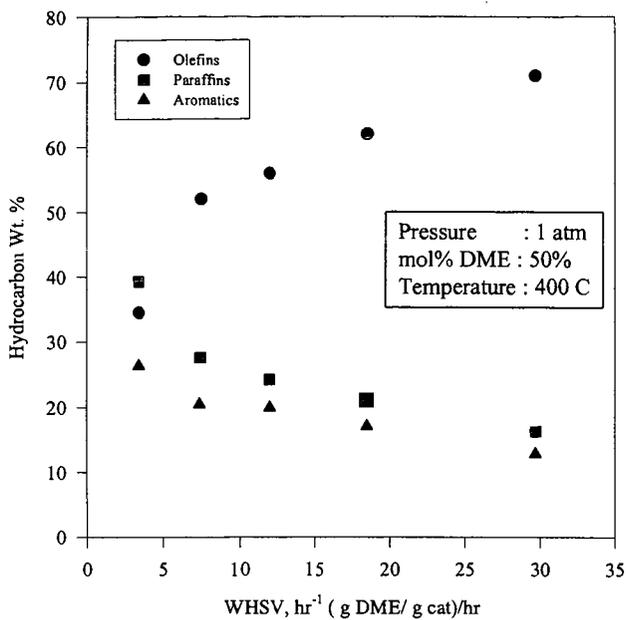


Figure 4. Effect of Space Velocity on Hydrocarbon Selectivity

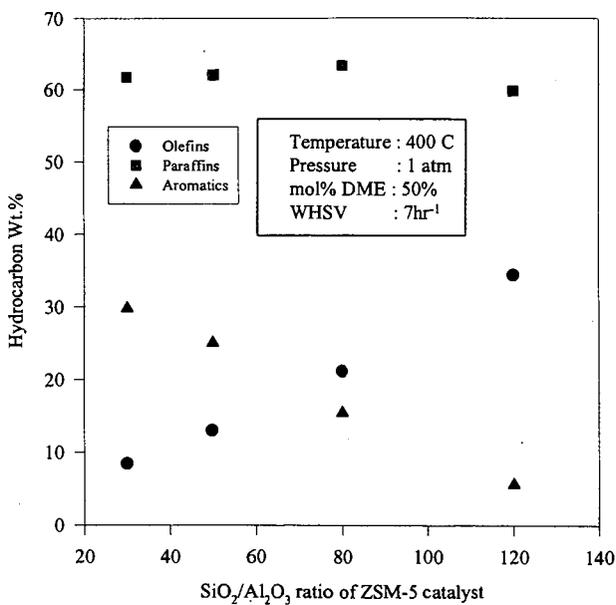


Figure 5. Effect of Zeolite Acidity on Hydrocarbon Selectivity