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CONVERSION OF ETHANE AND OF PROPANE TO HIGHER OLEFIN HYDROCARBONS

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INDEX

I. Task Description for 1992 3
II. Introduction 3
III. Highlights 3
IV. Progress of Studies 4

Reactions of Ethane 4
I. Task Description for FY 1992

Initial work on this project has shown that it is possible to convert ethane and propane in the presence of steam and oxygen over a catalyst comprising calcium-nickel-potassium oxide to both lower and higher hydrocarbons at temperatures in the range of 300-600° C. Major amounts of CO₂ are formed at the higher temperatures and conversions are relatively low at the lower temperatures. However, there are indications that the objective of preparing C₆ to C₁₂ olefins may be achieved by operating at intermediate temperatures and much higher space velocities than have thus far been used. It is proposed to do a systematic investigation making blank runs to distinguish between thermal and catalytic reactions and investigating modified catalysts such as calcium cobalt potassium oxide, calcium nickel sodium oxide, magnesium nickel potassium oxide, and others. A wide variety of operating conditions will be investigated. The catalytic reaction mechanism and the role of carbon on the catalyst will be investigated by experiments with carbon and oxygen isotopes.

II. Introduction

During the first quarter of FY 1992, experimental work was slowed down by mechanical problems with catalyst preparation. Plans have been drawn and equipment ordered for a pressure unit (500-1000 psi), since it is considered likely that pressure would favor the oligomerization of intermediate olefins to higher, liquid hydrocarbons. This unit will be assembled and put into operation during the second quarter.

III. Highlights

- A reevaluation of the data presented in the quarterly report of September 30, 1991, shows that in the presence of Ca₃NiK₀.₁ catalyst, the conversion of ethane in the presence of oxygen and steam results in lower CO₂ and higher ethylene selectivities than by purely thermal reaction.

- The work carried out thus far demonstrates that oxidative olefin coupling of ethane and propane is inhibited by the rapid oxidation of intermediates. This suggests either much shorter contact times or the presence of catalysts which would permit rapid conversion of the intermediates to higher hydrocarbons.
A series of experiments were performed over zeolite and metal-zeolite catalysts. Blank runs showed little ethane conversion in the absence of oxygen and steam. With oxygen high CO₂ selectivities prevailed. A vanadium-ZSM-5 catalyst gave the most promising results. At 550°C in the presence of oxygen and steam, an ethane conversion of ≈ 40% was obtained with 55% selectivity to ethylene, only 20% selectivity to CO₂ and about 20% selectivity to CO. About 3% higher hydrocarbons were formed.

Use of a Li-MgO catalyst did not result in interesting conversion.

IV. Progress of Studies

Reactions of Ethane

A number of catalysts were prepared. These included: HZSM-5; NaZSM-5; NiZSM-5; VZSM-5 and Li-MgO.

All of these were tested for the conversion of ethane either alone or in the presence of oxygen or oxygen and steam at an ethane space velocity of 4 mmoles/g cat/hr and over a temperature range of 350-600°C. The results are shown in Figs. 1-11.

With two exceptions, the reaction of ethane alone gave too low conversions over the whole temperature range to be meaningful (Fig. 1; 3; 7). In the case of NiZSM-5, there was appreciable conversion to methane (Fig. 5).

When ethane and oxygen were charged to HZSM-5 and NaZSM-5 (Fig. 2 and 4 resp), conversion increased at temperatures above 500°C. Surprisingly, selectivity to CO₂ decreased above 500°C while ethylene selectivity increased sharply. Conversion to methane was minimal.

The NiZSM-5 catalyst in the presence of oxygen (Fig. 6) was essentially a combustion and CO forming catalyst. The CO formation may be due to a Boudouart reaction between coke lay down and CO₂.

The vanadium ZSM-5 catalyst is the most interesting of this series. In the presence of oxygen (Fig. 8) appreciable conversion was obtained, which at temperatures above
500°C was increasingly to ethylene, while COx declined and methane formation was minimal. When steam was added to the feed (Fig. 9) the only change was a small increase in ethylene selectivity. Over this catalyst a small amount (4%) of higher hydrocarbons is formed.

The Li-MgO catalyst was tested because it has been widely described in the literature for the oxidative coupling of methane at 700-850°C. Ethane and oxygen gave good conversions at 600° (Fig. 10) with about equal selectivities (40%) to ethylene and COx. In the presence of oxygen and steam (Fig. 11) there was a severe decline in conversion compared to the run with C2H6 plus oxygen and a major increase in COx.

It is apparent that oxydehydrogenation of ethane to ethylene is easily accomplished in almost all cases, but that the olefin is more easily oxidized than polymerized. Since it is known that propylene is easier to polymerize than ethylene, a few of the experiments described will be repeated with a propane charge.
Reaction of Ethane over H-ZSM5 Catalyst

![Graph showing conversion and selectivity over temperature.

- Conv. %
- C1
- C2
- Others

Figure 1
Reaction of Ethane with Oxygen over H-ZSM5 Catalyst

![Graph showing conversion and selectivity of various products with temperature from 440 to 560°C. The graph includes lines for different products such as Conv.% (conversion percentage), Cl\(^{-}\), C\(_2\), CO, CO\(_2\), and O\(_2\)/Conv.% (oxygen conversion percentage).]
Reaction of Ethane over Na-ZSM-5 Catalyst

Figure 3
Reaction of Ethane with Oxygen over Na-ZSM5 Catalyst

Figure 4

Conv.% 

Cl⁺ 

C₂ 

CD 

CO₂ 

O₂/Conv.% 

Others 

Temp. °C
Reaction of Ethane over Ni-ZSM-5 Catalyst

Figure 5
Reaction of Ethane with Oxygen over Ni-ZSM5

Figure 6
Reaction of Ethane over V-ZSM5 Catalyst

Figure 7
Reaction of Ethane with Oxygen over V-ZSM5 Catalyst

Figure 8

Temp. °C

Conversion & Selectivity %
Reaction of Ethane with Oxygen in the Presence of Steam over V-ZSM5 Catalyst

Figure 9
Reaction of Ethane with Oxygen over Li/MgO (YFC-0716)

Figure 10
Reaction of Ethane with Oxygen in the Presence of Steam over Li/MgO (YFC-0716) Catalyst

Figure 11