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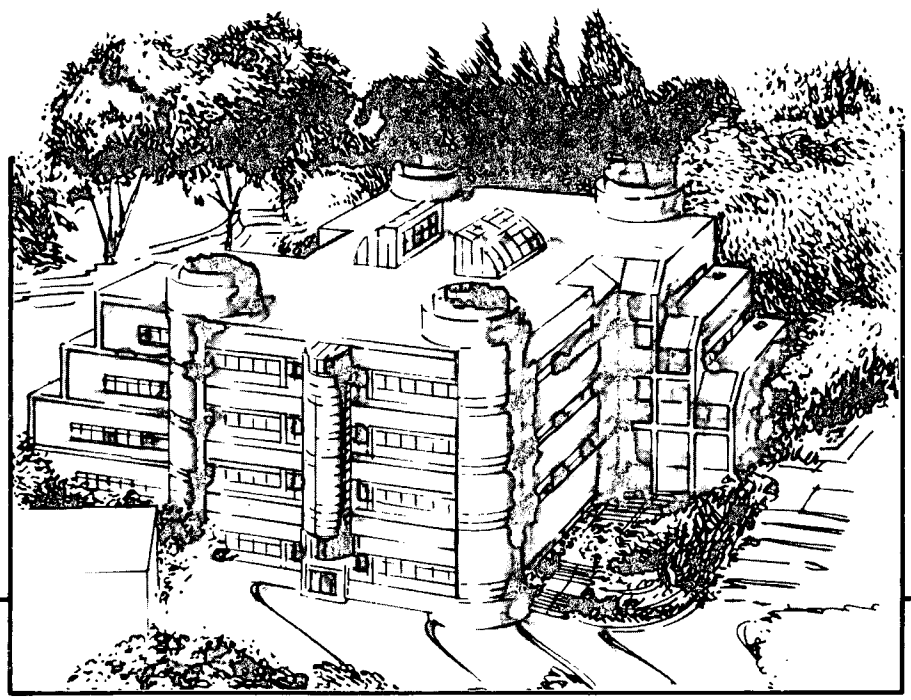
Quarterly Report
April 1–June 30, 1991

H. Heinemann and G.A. Somorjai

June 1991



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QUARTERLY REPORT

April 1, 1991 - June 30, 1991

CONVERSION OF ETHANE AND OF PROPANE TO HIGHER OLEFIN HYDROCARBONS

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I. Task Description for FY 1991

It is the purpose of this work to extend recent findings of oxidative methane coupling to the coupling of paraffinic hydrocarbons such as ethane and propane to produce C_4 respectively C_6 and higher hydrocarbons. Variables which have been shown to influence the olefin/paraffin ratio of the product will be investigated to optimize olefinic products. A study of the reaction mechanisms is to be undertaken on the basis of which improved catalysts will be synthesized.

II. Introduction

- Dr. Y..-F. Chang joined the group as a post-doctoral fellow in early June and will be working exclusively on this project. A few preliminary experiments have been carried out.

III. Highlights

- Ethane was charged together with oxygen and steam to a Ca-Ni-K oxide catalyst at three temperatures (300, 450 and 600°C) and atmospheric pressure.
- At 300°C conversion was very low (<1%). Only hydrocarbons were found in the product, no carbon oxides. The major hydrocarbon was methane, the yield of which decreased with time on stream with a corresponding increase in propylene and ethylene.
- At 450°C conversion reached 60-70%, selectivity to hydrocarbons was 50% or less (mostly CH_4) with the remainder being carbon oxides.
- At 600°C there was almost complete conversion of ethane to methane and carbon oxides with only very small amounts of ethylene. There appeared to be substantial coke deposition on the catalyst.
- It is apparent from these results that while both dehydrogenation to ethylene and disproportionation to methane and higher hydrocarbons than C_2 can occur, temperatures of 600°C are too high and other process variables have to be explored.
- A single run with propane feed at 600°C showed continuous catalyst deactivation and gave methane and CO_x as major products with propylene being the largest constituent of C_2-C_6 hydrocarbons.

IV. Progress of Studies

A diagram of the experimental set-up is given in Fig. 1. The catalyst used was a ternary oxide of calcium, nickel and potassium in atomic ratio of 3:1:0.5 prepared from the nitrates and after calcination treated for 8 hours in flowing oxygen at 680°C. Between 0.5 and 1 g of catalyst was charged to the reactor. Ethane (or propane), oxygen and water were fed to the reactor in a molecular ratio of 3:1:6. The ethane feed rate was 4 mmole/g of catalyst/hr. This results in a long contact time. Catalyst temperature was maintained at 300, 450 and 600°C, resp. Products were analyzed by G.C. Carbon balances were obtained around the unit. Poor carbon balances indicate carbon deposition on the catalyst.

Figure 2 shows that conversion increased with temperature, but was very low at 300°C. Carbon balances are given in Fig. 3. While a good carbon balance was obtained over 10 hrs. at 300°C, the balances at 450 and 600°C were lower at the start and declined further during the first 3 hrs., probably indicating carbon deposition on the catalyst.

Figure 4 presents selectivities to hydrocarbons and to CO_x at 300°C as well as selectivities to CH_4, C_2H_4 and C_3H_6. It is apparent that at the low conversion (Fig. 3) noticeable amounts of C_2H_4 and C_3H_6 were produced.

Figures 5 and 6 present the same information for operation at 600°C. While ethane conversion increased with temperature, methane became increasingly the major product. At 600°C appreciable amounts of CO appeared in the product, indicating steam reforming.

In summary these early data on ethane conversion at conditions close to those used in methane oxidative coupling indicate that much milder conditions will be needed to produce C_2 and higher olefins.

A single run was made with a propane feed at the same rates over a Ca-Ni-K-oxide (atomic ratio 3:1:0.1) and 600°C. Table 1 summarizes the results, which while somewhat promising should be qualified by the fact that this was a very preliminary experiment.

TABLE 1

Propane Coupling
$Ca_3 Ni_1 K_{0.1}$ Catalyst
600°C; C_3H_6:O_2:H_2O = 3:1:6

Time min	C_3H_8 conv.%	Product Distribution								
		CO_x %	CH_4 %	C_2H_4 %	C_2H_6 %	C_3H_8 %	C_3H_6 %	C_4 %	C_5 %	C_6 %
60	30	25	40	5	5	--	10	6	2	7
120	22	30	35	6	4	--	12	4	3	6
180	15	35	30	5	7	--	14	2	2	5

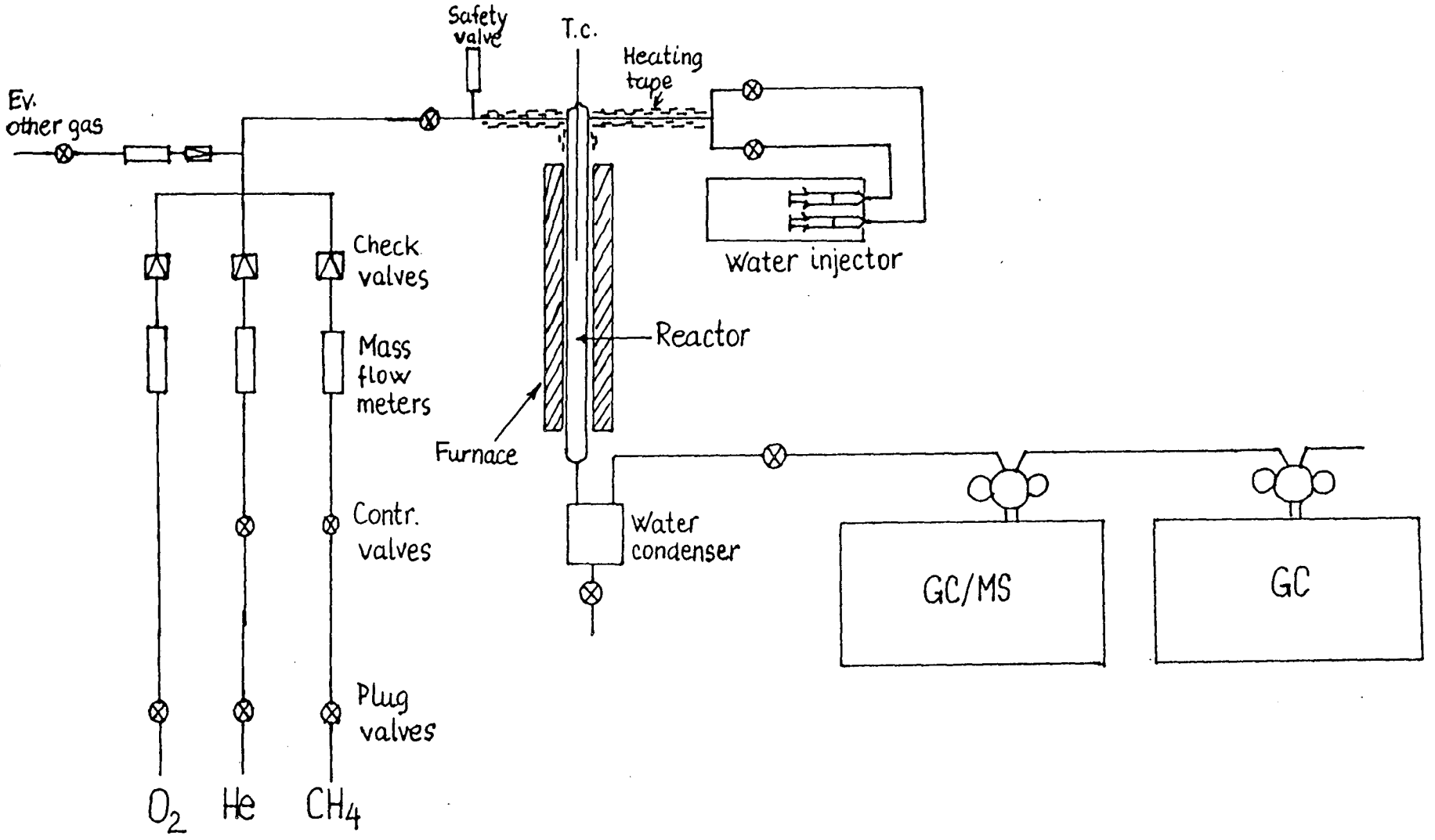
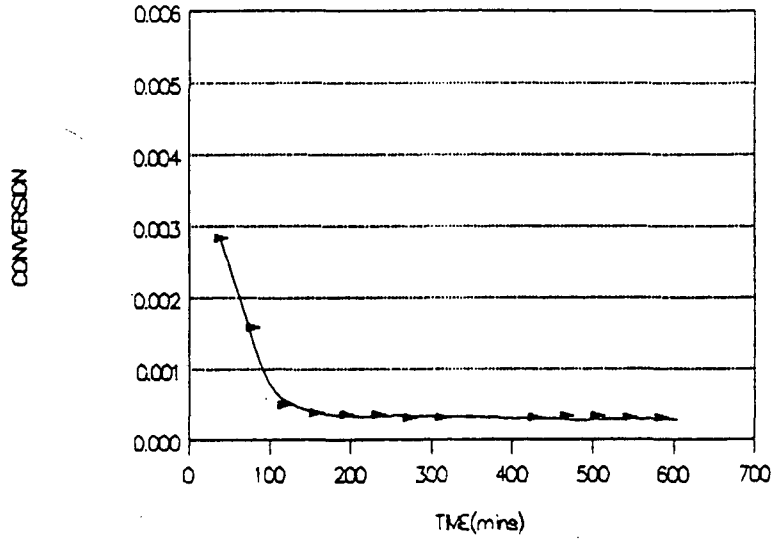
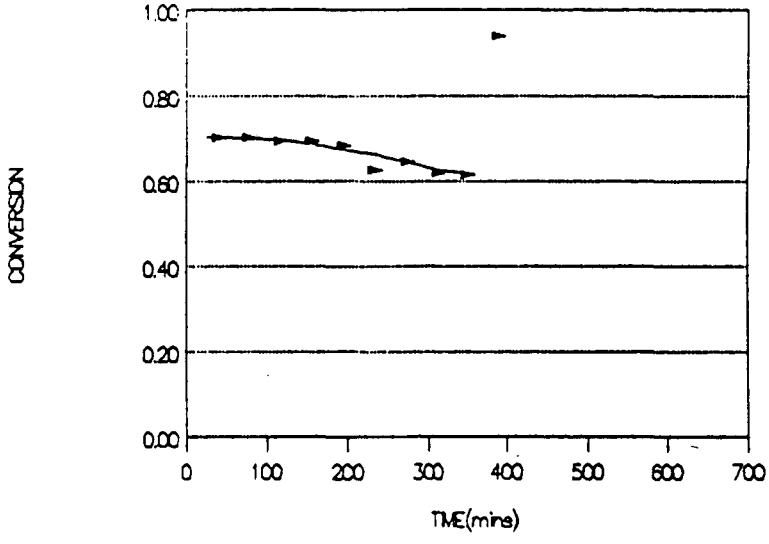

Safety valve
T.c.
Heating tape
Ev. other gas
Check valves
Water injector
Mass flow meters
Reactor
Furnace
Contr. valves
Water condenser
GC/MS
GC
Plug valves
O_2
He
CH_4

Figure 1

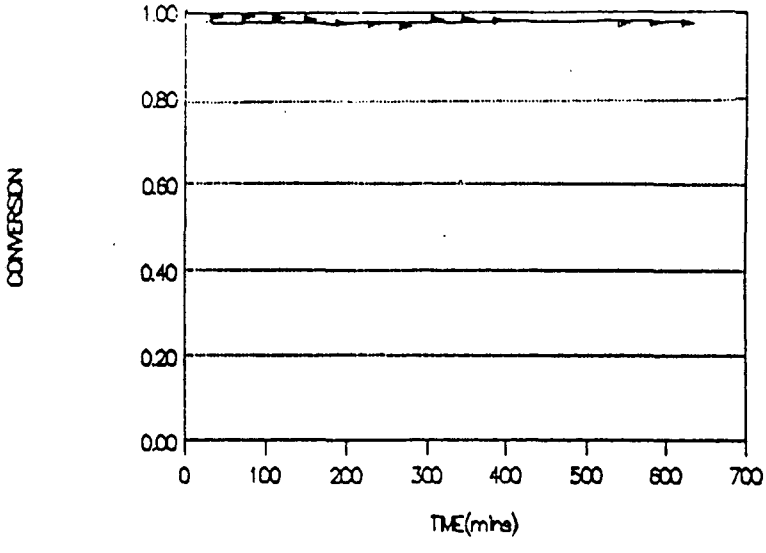
Figure 2
Conversion of Ethane



300°C

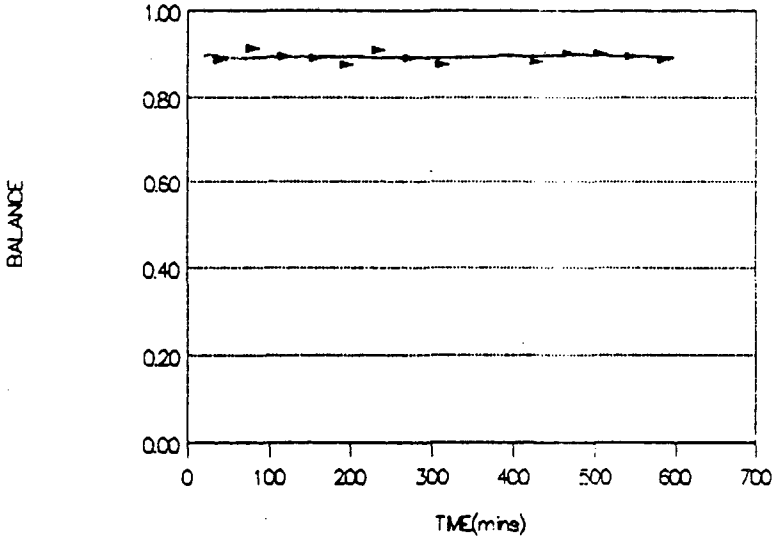


450°C

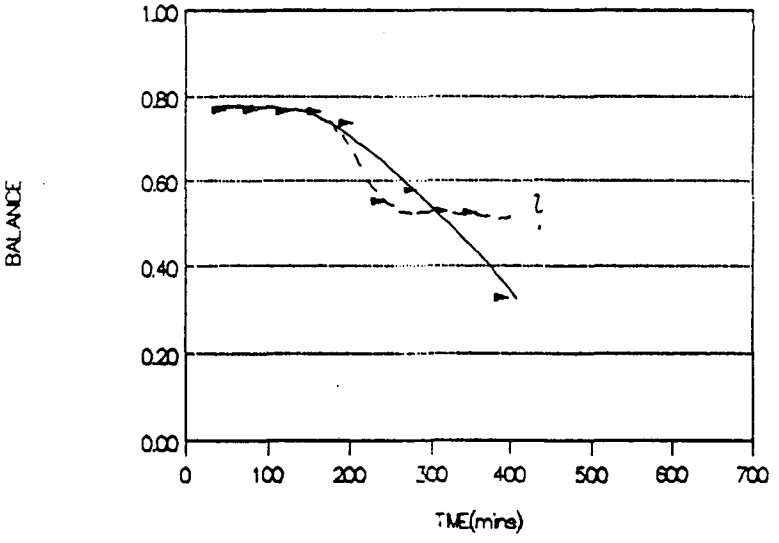


600°C

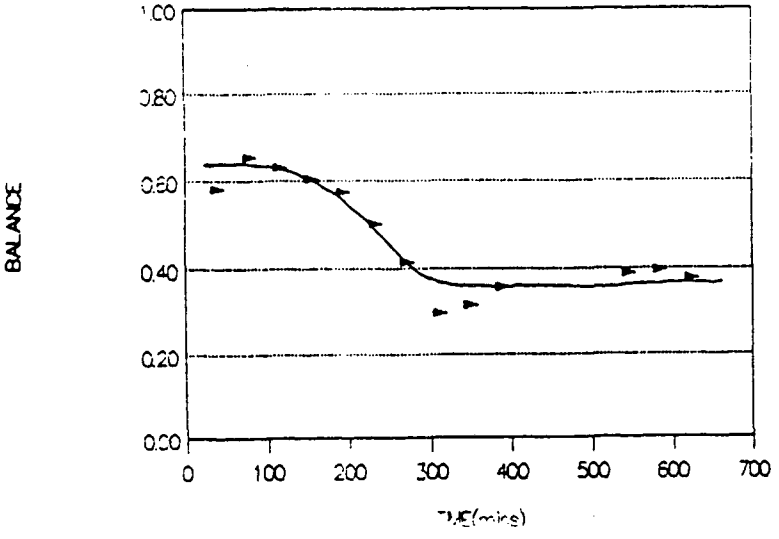
Figure 3
Carbon Balances



300°C

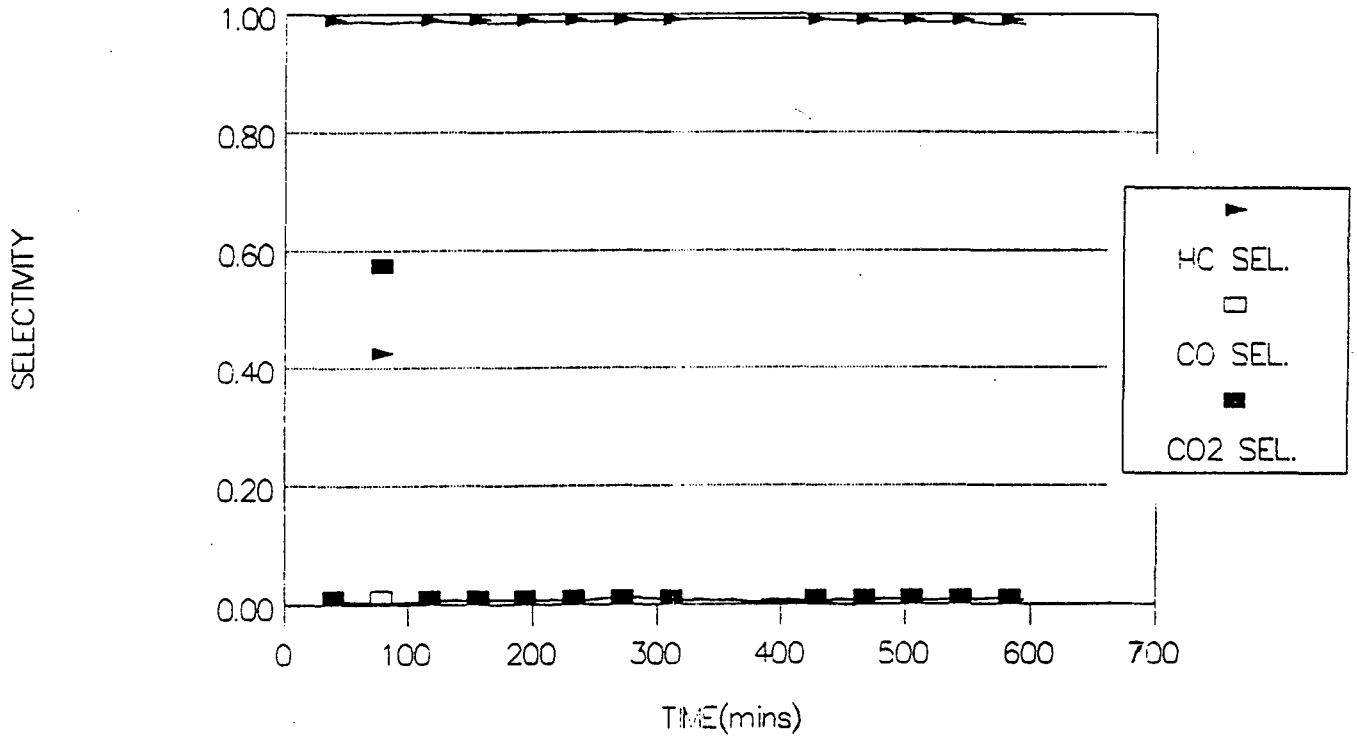


450°C



600°C

Figure 4
Selectivities of Ethane Conversion at 300°C



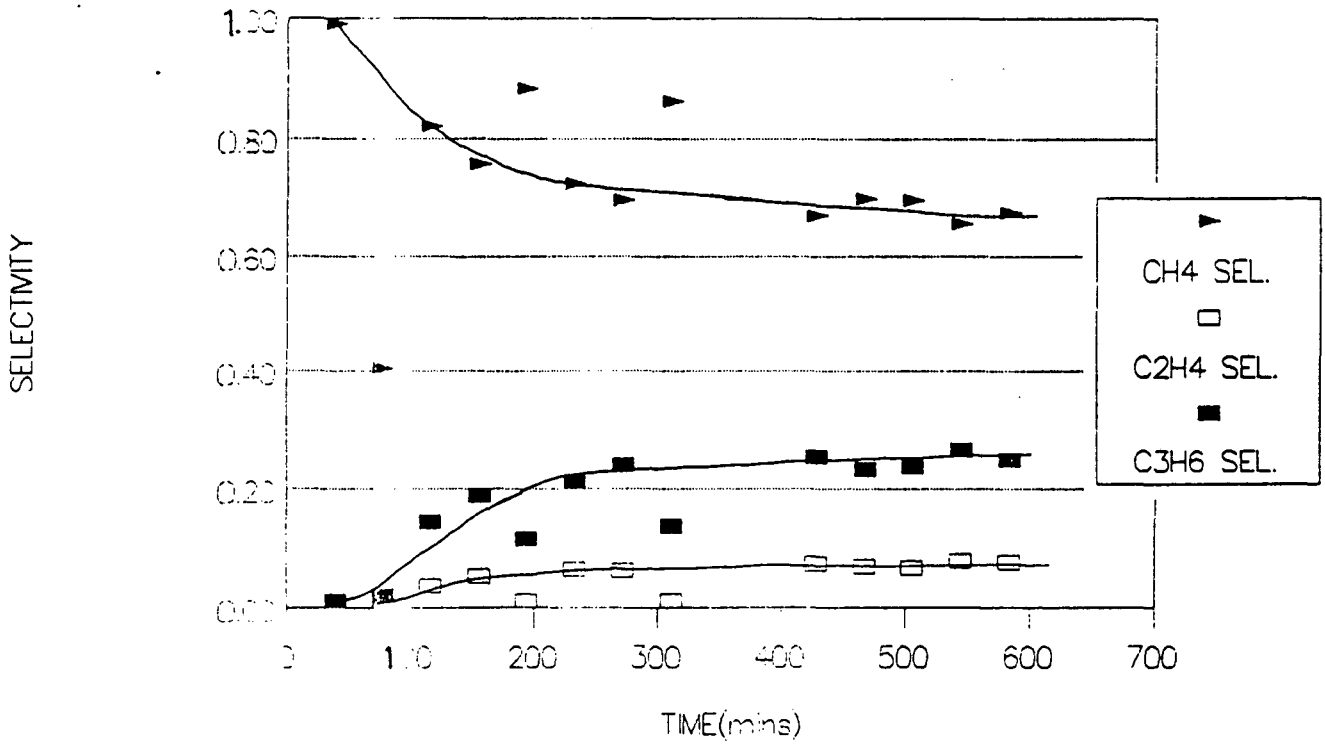
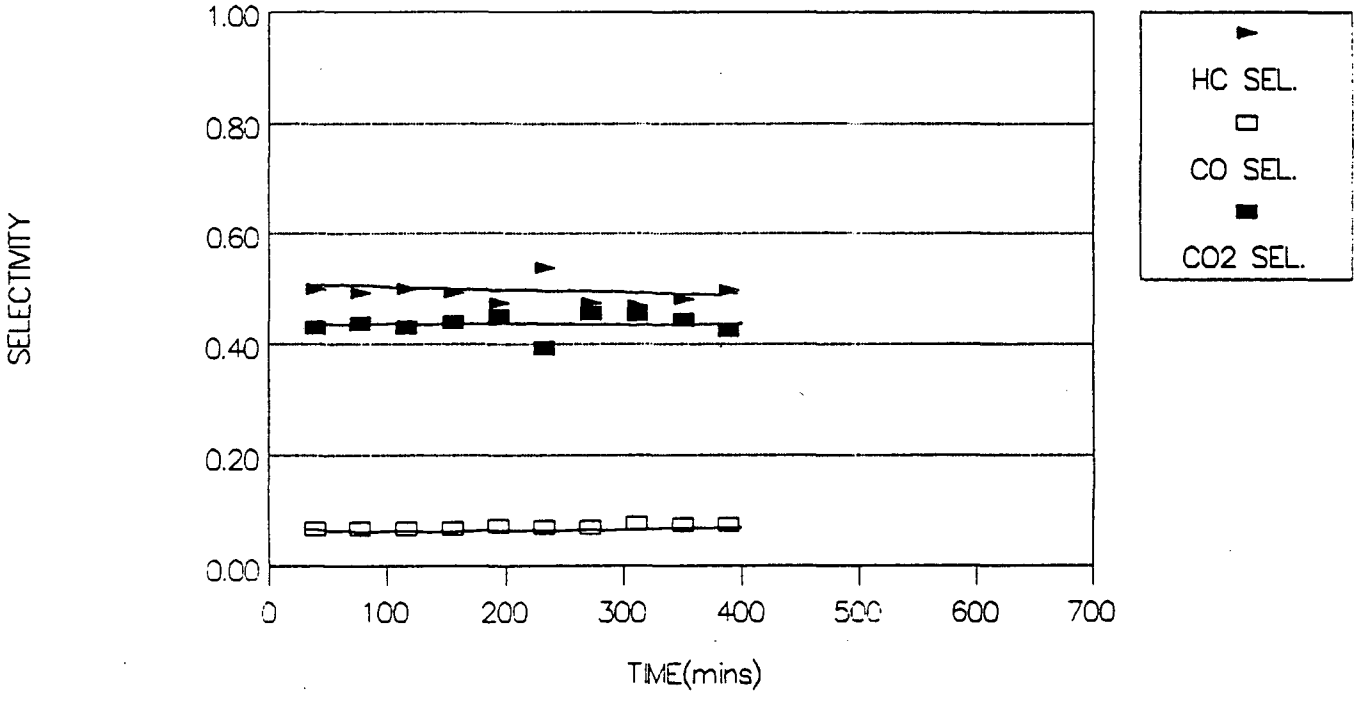


Figure 5
Selectivities of Ethane Conversion at 450°C



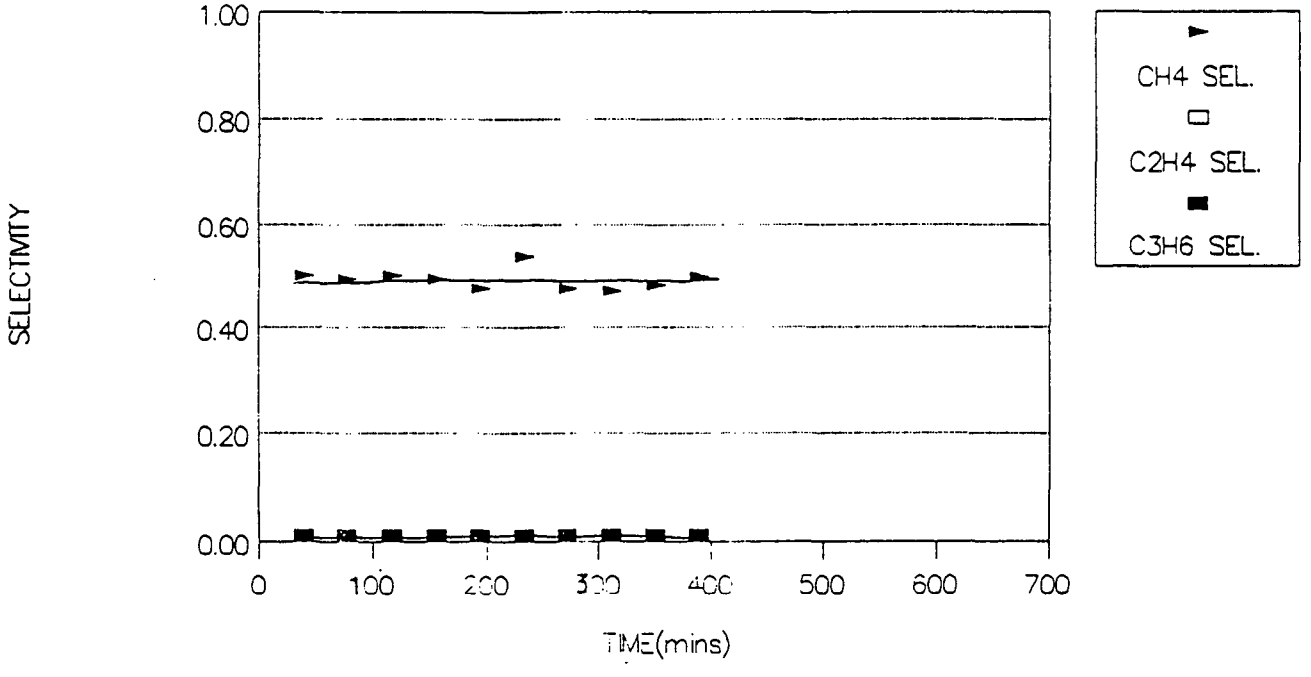
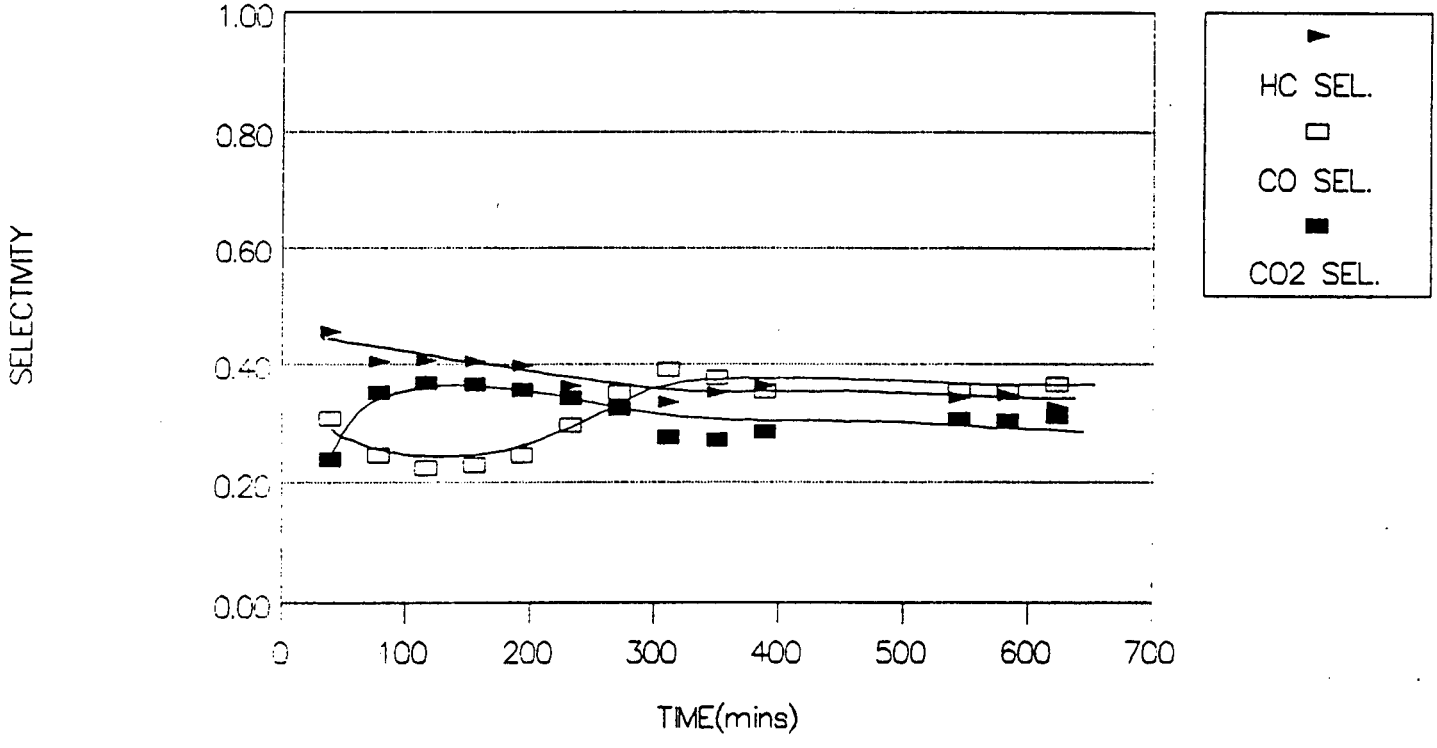
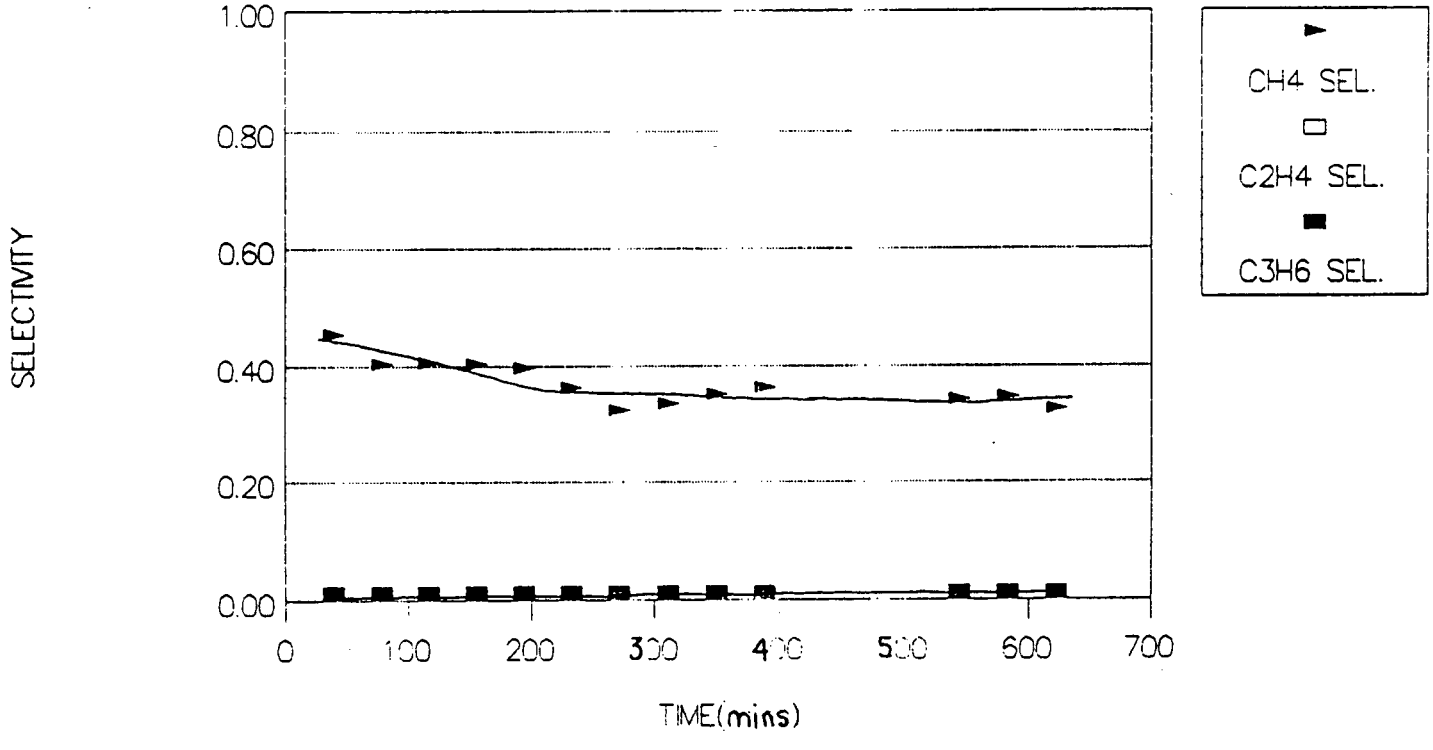


Figure 6
Selectivities of Ethane Conversion at 600°C





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