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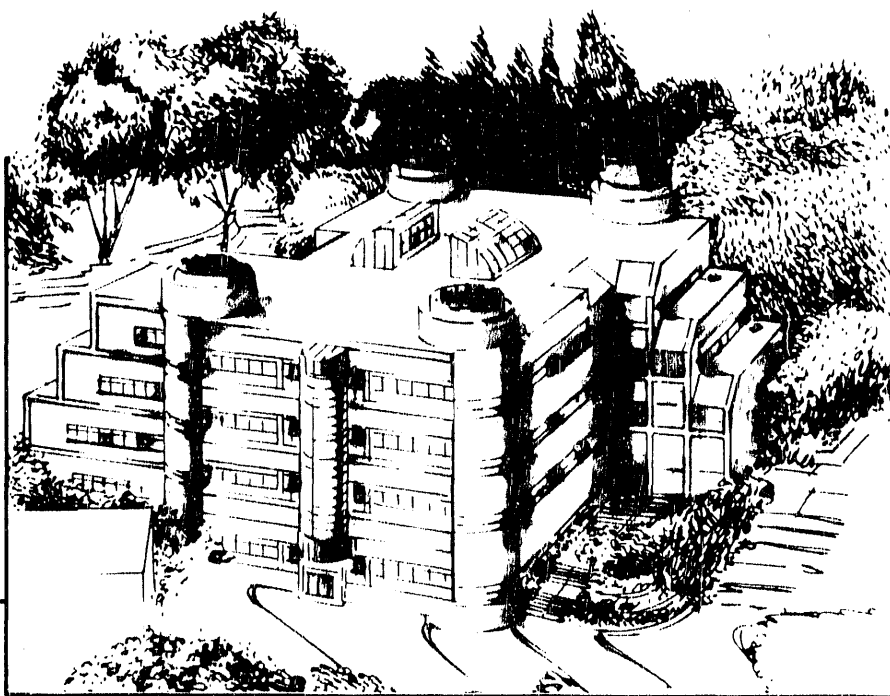
Conversion of Ethane and of Propane to Higher Olefin Hydrocarbons

Quarterly Report

July 1–September 30, 1991

H. Heinemann and G.A. Somorjai

October 1991



Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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QUARTERLY REPORT

July 1, 1991 - September 30, 1991

**CONVERSION OF ETHANE AND OF PROPANE
TO HIGHER OLEFIN HYDROCARBONS**

Principal Investigators: Heinz Heinemann
Gabor A. Somorjai

Center for Advanced Materials
Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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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. Highlights

- Purely thermal reactions for the conversion of ethane were carried out in an empty and in a quartz chip filled reactor over a temperature range of 300°-800° C in the absence and presence of oxygen and oxygen plus water.
- Ethane alone shows no conversion below 600°C and some conversion to CH_4 and very little C_2H_4 at 700° and 800°C.
- Ethane and oxygen produce CO_2 as the major product above 400°C. The additional presence of water does not appreciably change this picture.
- Converting ethane with oxygen and water over a $Ca_3Ni_{11}K_{0.1}$ catalyst at very low space velocity gave increasing conversion with temperature, primarily CO_2 production and a small amount of C_{3+} hydrocarbons. The CO_2 production was decreased and slightly more C_3 hydrocarbons were produced when the potassium concentration of the catalyst was increased.
- Activation energies have been calculated for the various ethane conversion reactions.
- It appears that the $CaNiK$ oxide catalyst is not suited for oxidative ethane coupling at the conditions thus far investigated. The indications are that much shorter contact times are required to prevent oxidation of intermediates.

- Blank runs with propane and oxygen in the absence of a catalyst have shown significant reaction at temperatures as low as 400°C.

III. Progress of Studies

A systematic study was undertaken in an empty reactor to determine the purely thermal reactions (free radical reactions) of various feeds at a series of temperatures. In order to evaluate surface effects, several of the experiments were repeated in the presence of quartz chips in the reactor. This set of experiments will serve as a background to differentiate catalytic from thermal reactions.

a) Reactions of Ethane

Figure 1 presents information on the reaction of ethane alone in an empty reactor. Essentially no conversion is obtained below 600°C. At 700° and 800°C conversion increases to 20, resp. 70% with the major products being ethylene and methane. About 10% higher hydrocarbons were obtained at 800°. Ethylene production declined with temperature. In a quartz chip containing reactor, the results (Fig. 2) are similar, but more methane and less ethylene are produced at the high temperatures. Some higher hydrocarbons are found at low temperature.

Figures 3A and 3B show results from experiments with a 3:1 molar mixture of ethane and oxygen. Figure 3A is for experiments in the quartz chip reactor, 3B with CaNiK catalyst. In the absence of catalyst, CO₂ shows up as a major product at temperatures above 400°C; however, CO₂ yield declines with temperature, and ethylene yield increases. Methane is found above 550°C. There is no CO productivity. The decrease of CO₂ at higher temperatures may be due to coke deposition on the quartz chips and reactor walls. Comparing Figs. 3A and 3B, it appears that the catalyst inhibits CO₂ formation, sharply reduces conversion and initially produces some higher hydrocarbons.

Figure 4 is a presentation of a blank run with ethane, oxygen and water and the results are almost identical with those in Fig. 3, except that there is some CO production.

Figures 5-9 show conversion and selectivity as a function of time on stream using a standard calcium-nickel-potassium oxide catalyst, which is active for CH₄ oxidative

coupling, at temperatures of 350, 400, 450, 500 and 550°C. The CH₄:O₂:H₂O molar ratio was 3:1:6 and the CH₄ feed rate was 0.4 mmole/g catalyst/hr. Conversions were very low below 550°C. The data are summarized in Fig. 10. The major product at all temperatures was CO₂, C₂H₄ being the next largest product. Relatively little CH₄ and very small quantities of higher (C₄) hydrocarbons were initially observed. Comparing Fig. 10 with Fig. 4 (empty reactor), it appears that the catalyst suppresses conversion and C₂H₄ formation and increases production of methane.

Figure 11 shows data obtained with a Ca-Ni-K oxide catalyst containing .5 instead of .1% potassium. It differs from Fig. 10 in showing much higher conversion, and initially higher C₃₊ production along with lower CO₂ formation.

Comparing the strictly thermal runs (Fig. 4) with the catalytic run with Ca₃Ni₁K_{0.5} (Fig. 11), it is apparent that at 600°C the catalyst gives higher conversion (100% vs 60%) less CO₂ and more CH₄. Very little C₃₊ is produced in either case.

An experimental magnesium-iron-potassium oxide catalyst was essentially inactive (Fig. 12).

Arrhenius diagrams were obtained for all cases and the activation energies are presented in Table 1.

TABLE 1

Activation Energies for Ethane Conversion

Reactor Content	Feed	Activation Energy KJ mol ⁻¹
Empty	C ₂ H ₆	108
Quartz Chips	C ₂ H ₆	155
Empty	C ₂ H ₆ + O ₂	53
Empty	C ₂ H ₆ + O ₂ + H ₂ O	33
Ca ₃ Ni ₁ K _{0.1}	C ₂ H ₆ + O ₂	124
Ca ₃ Ni ₁ K _{0.1}	C ₂ H ₆ + O ₂ + H ₂ O	55

At this time it is concluded that under standard methane coupling, our standard catalyst is not a good catalyst for producing higher hydrocarbons at the conditions tested thus far. It inhibits, however, the high CO₂ formation observed in a purely thermal reaction. There are indications that the space velocity used is too low and that secondary reactions may take place. Further work will investigate this.

b) Reactions of Propane

Reactions of propane with oxygen in empty ceramic tubular reactor and reactor half filled with quartz chips have been studied at temperatures 400-600°C. Results are contained in Tables 2 and 3. The reaction between propane and oxygen is significant at temperatures as low as 400°C. Increase of reaction temperature results in a dramatic increase in propane conversion. The use of quartz chips does not seem to induce a noticeable increase in the extent of reaction between propane and oxygen. Thus, quartz chips can be used as an inert filling material for study of reaction of propane with oxygen.

Table 2**Results of Reaction of Propane with Oxygen in Empty Reactor ^a**

Temperature/°C	Conversion %	<u>Selectivity %</u>	
		Hydrocarbons	CO _x
400	2.3	33.3	66.7
500	36.5	43.3	56.7
600	68.9	85.3	14.7

a, Propane : 3.0 cm³ min⁻¹; oxygen: 1.0 cm³ min⁻¹.

Table 3

**Results of Reaction of Propane with Oxygen in a
Ceramic Reactor Filled with Quartz Chips a,b**

Temperature/°C	Conversion %	<u>Selectivity %</u>	
		Hydrocarbons	CO _x
400	13.3	19.5	80.5
500	28.0	47.7	52.3
600	62.5	70.8	29.2

a, Propane : 3.0 cm³ min⁻¹; oxygen: 1.0 cm³ min⁻¹; b, the reactor half filled with quartz chips.

Reaction of Ethane in Empty Reactor

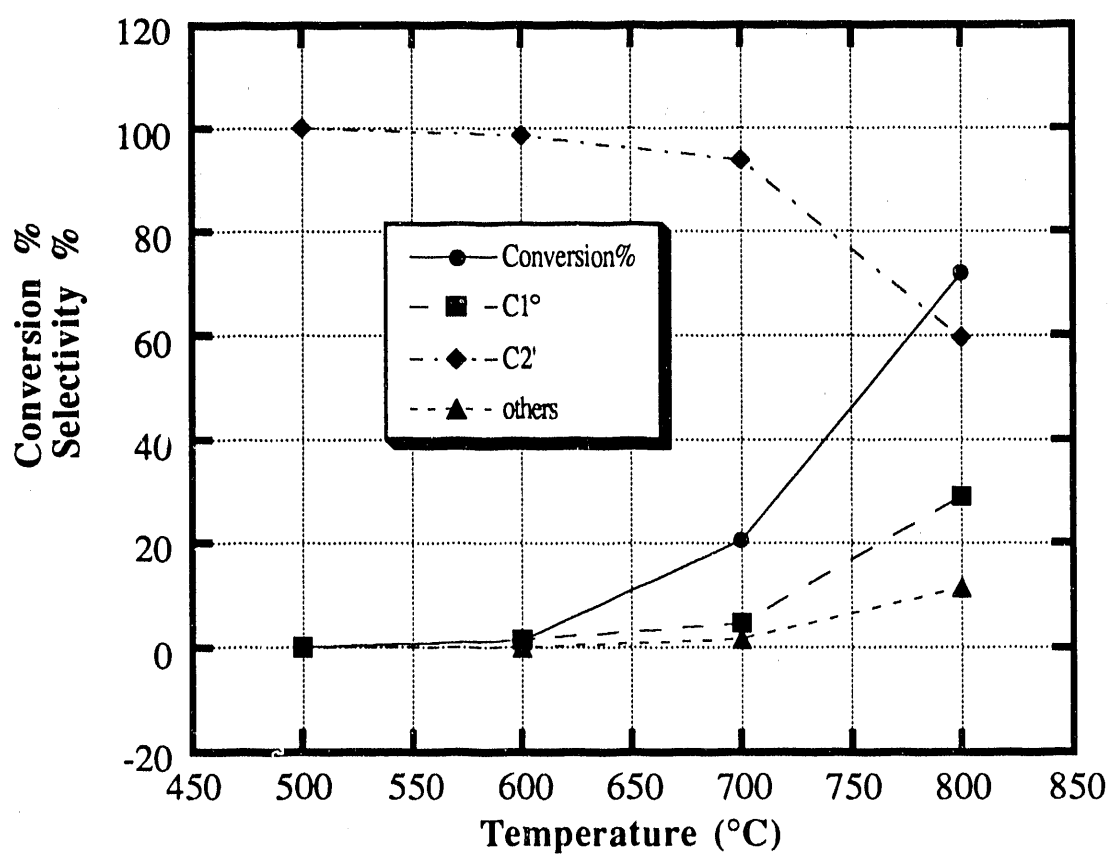


Figure 1

**Reaction of Ethane in Reactor
(partly filled with quartz chips)**

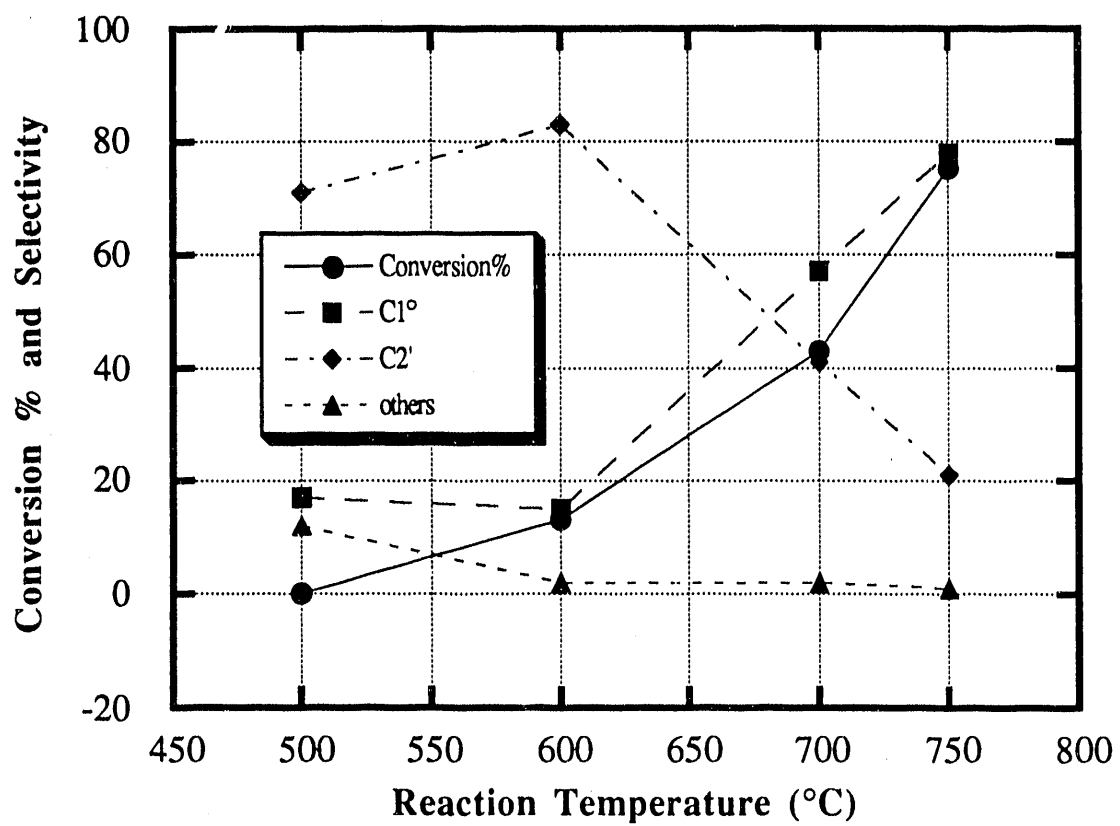


Figure 2

$C_2^o + O_2$ /Empty Reactor (half filled with ceramic chips)

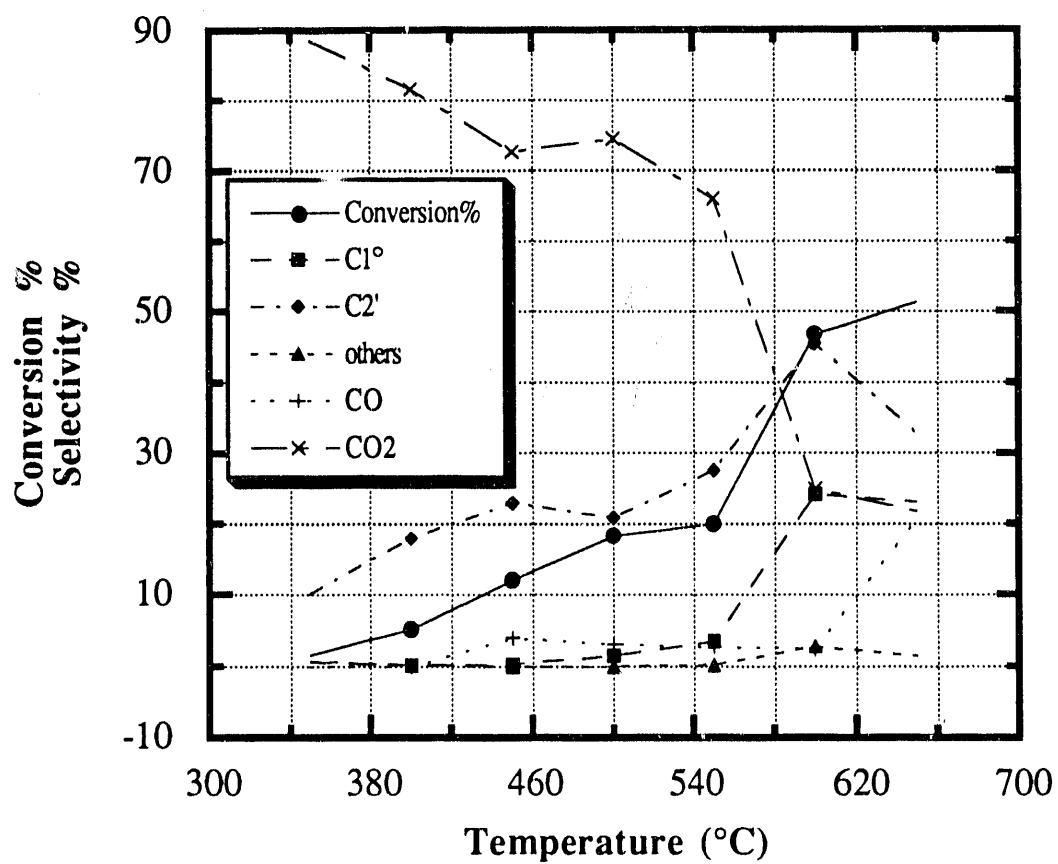


Figure 3A

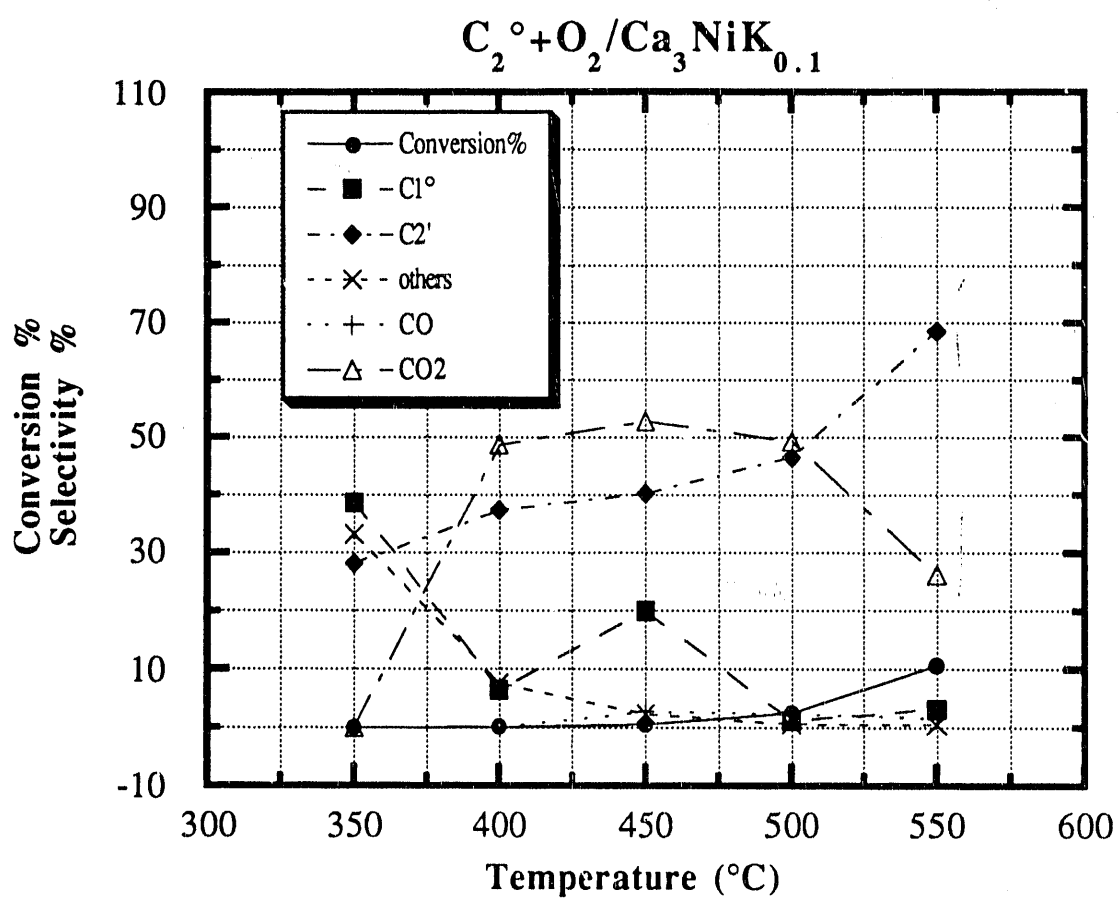


Figure 3B

$C_2^o + O_2 + H_2O$ /Empty Reactor (half filled with ceramic chips)

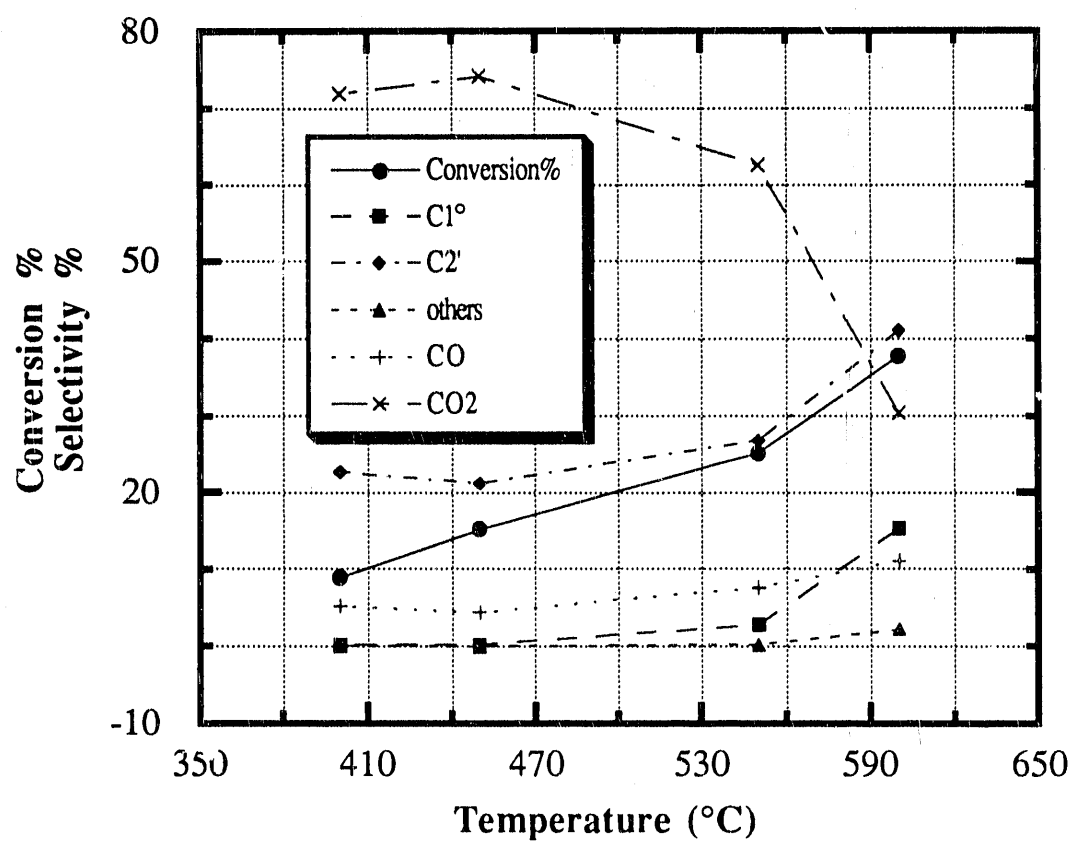


Figure 4

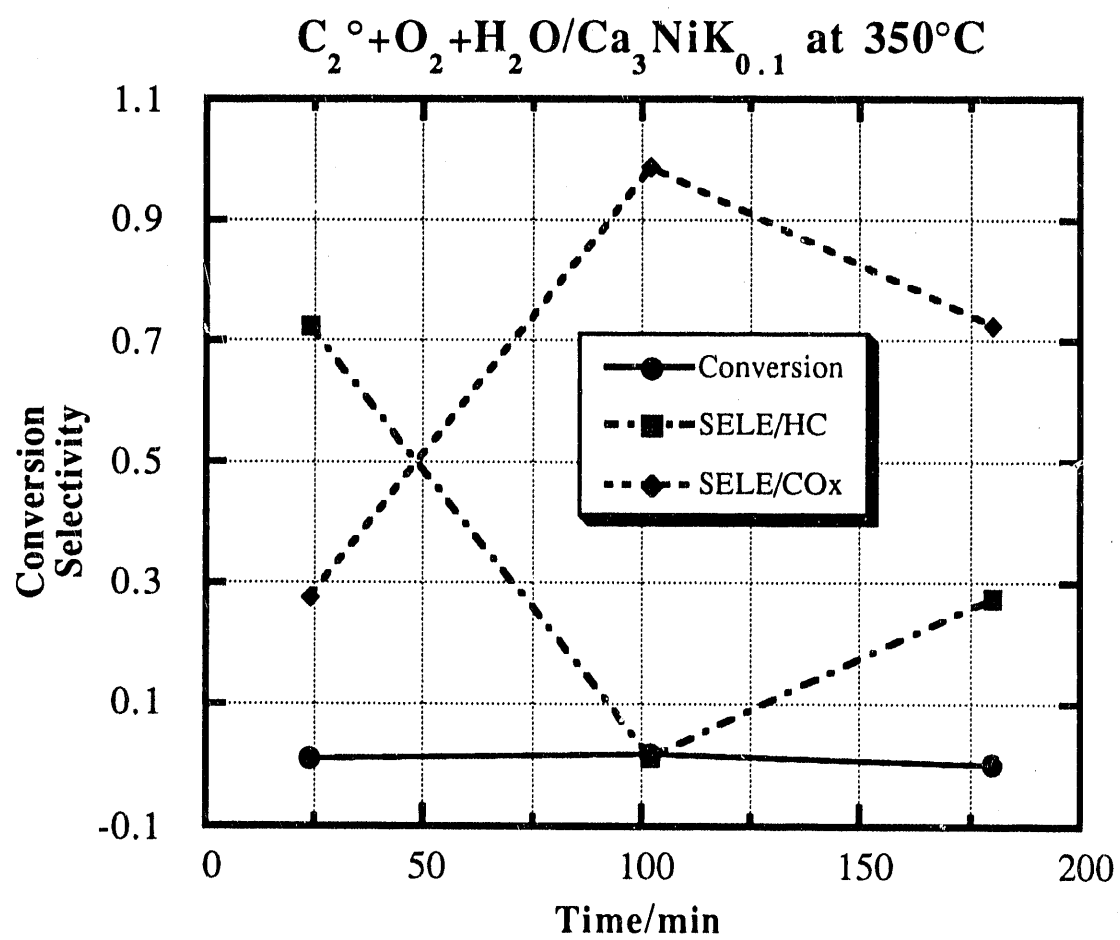


Figure 5

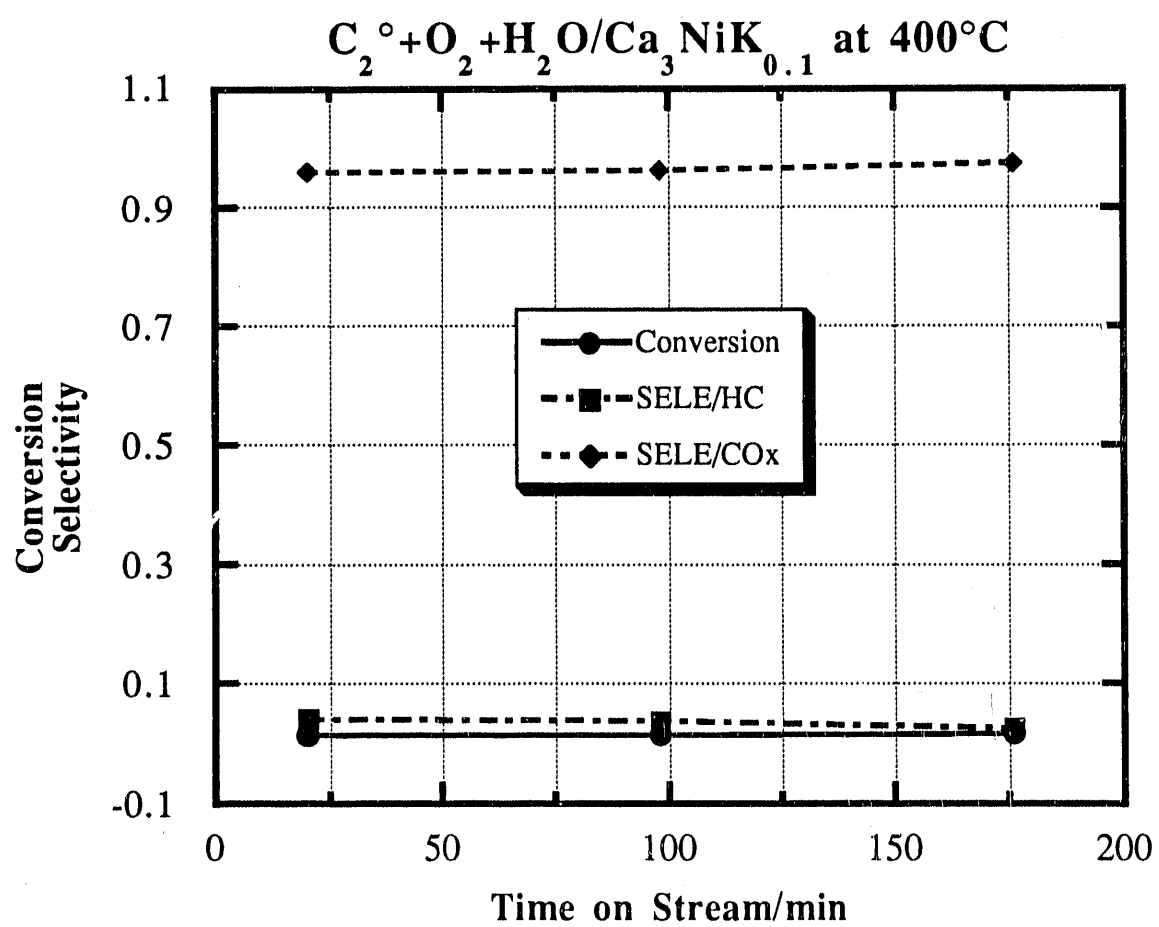


Figure 6

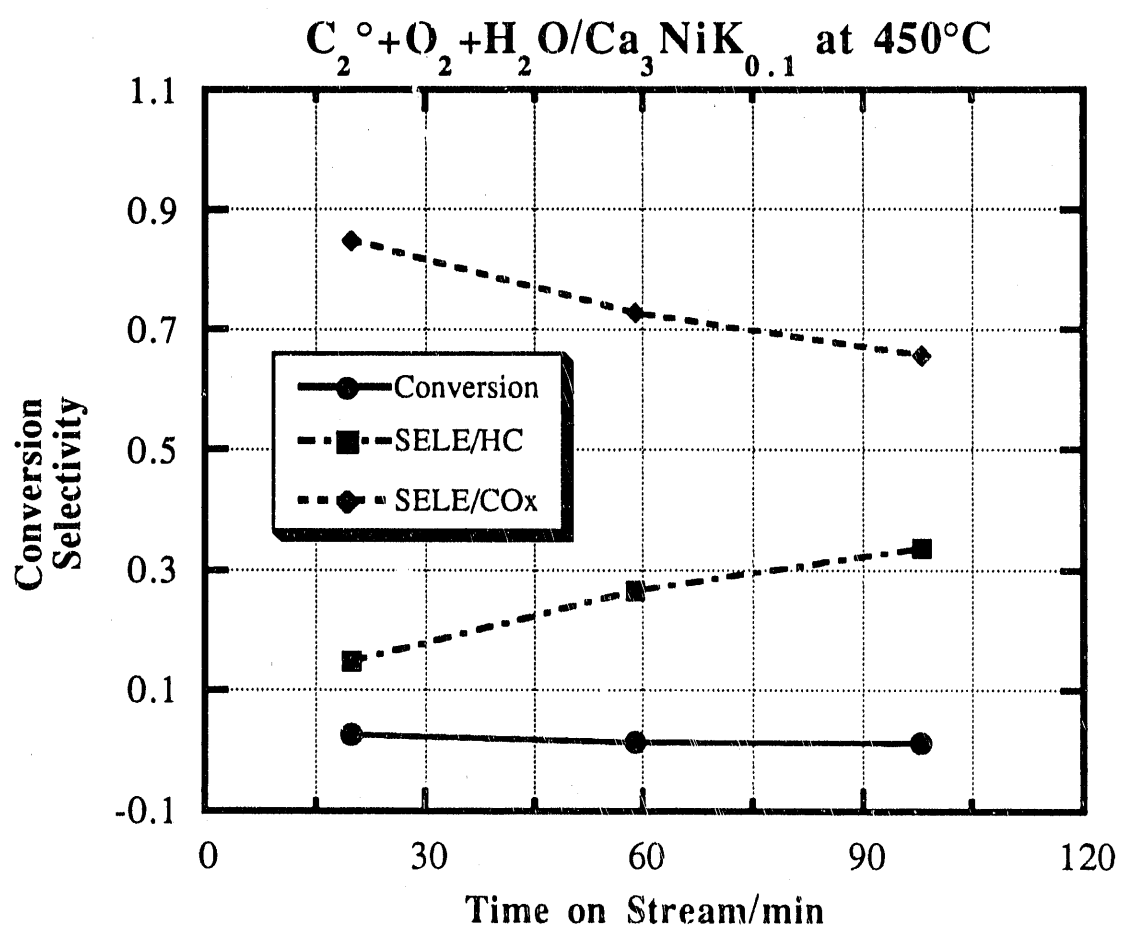


Figure 7

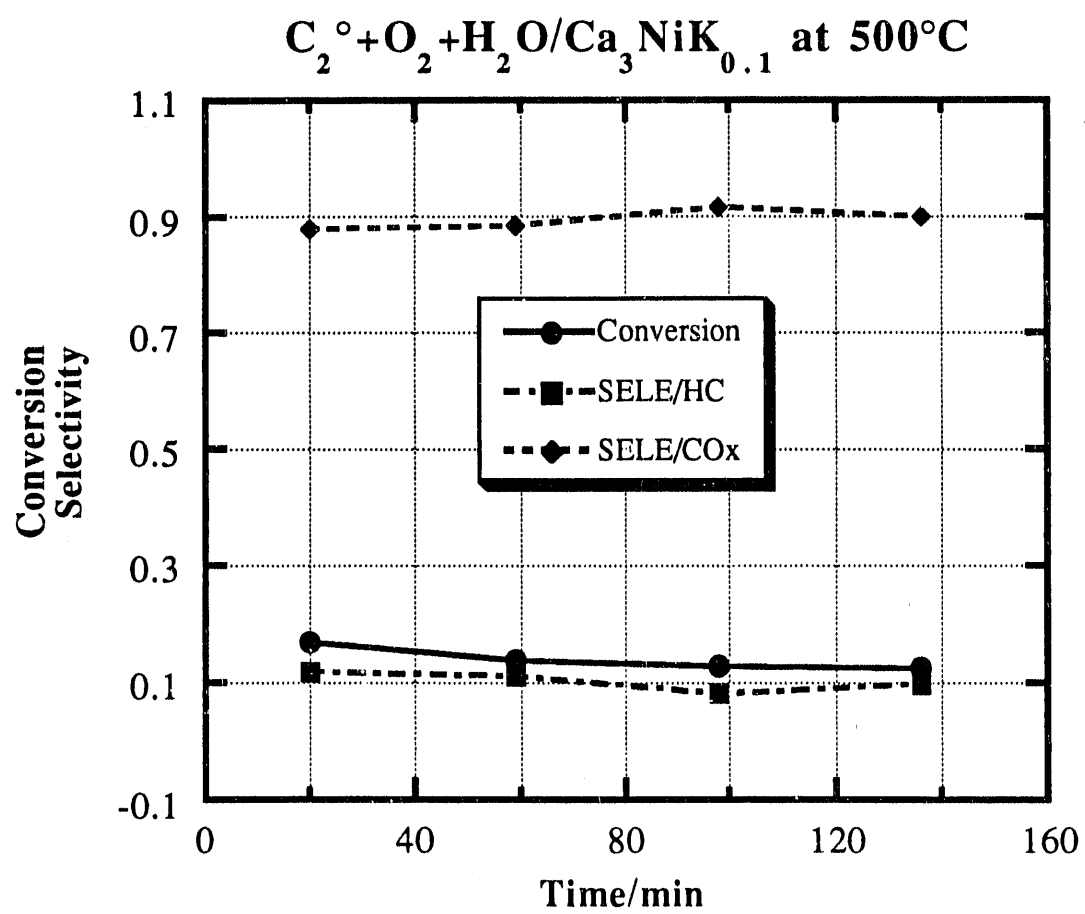


Figure 8

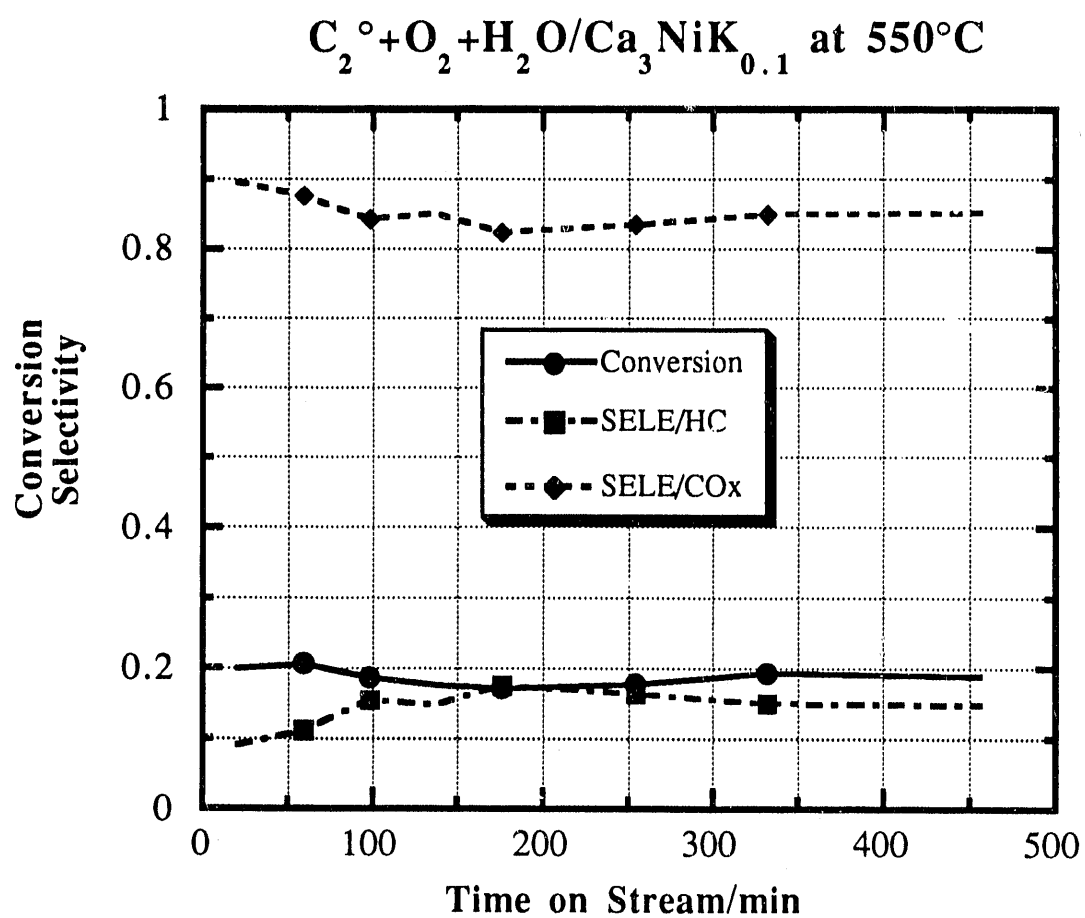


Figure 9

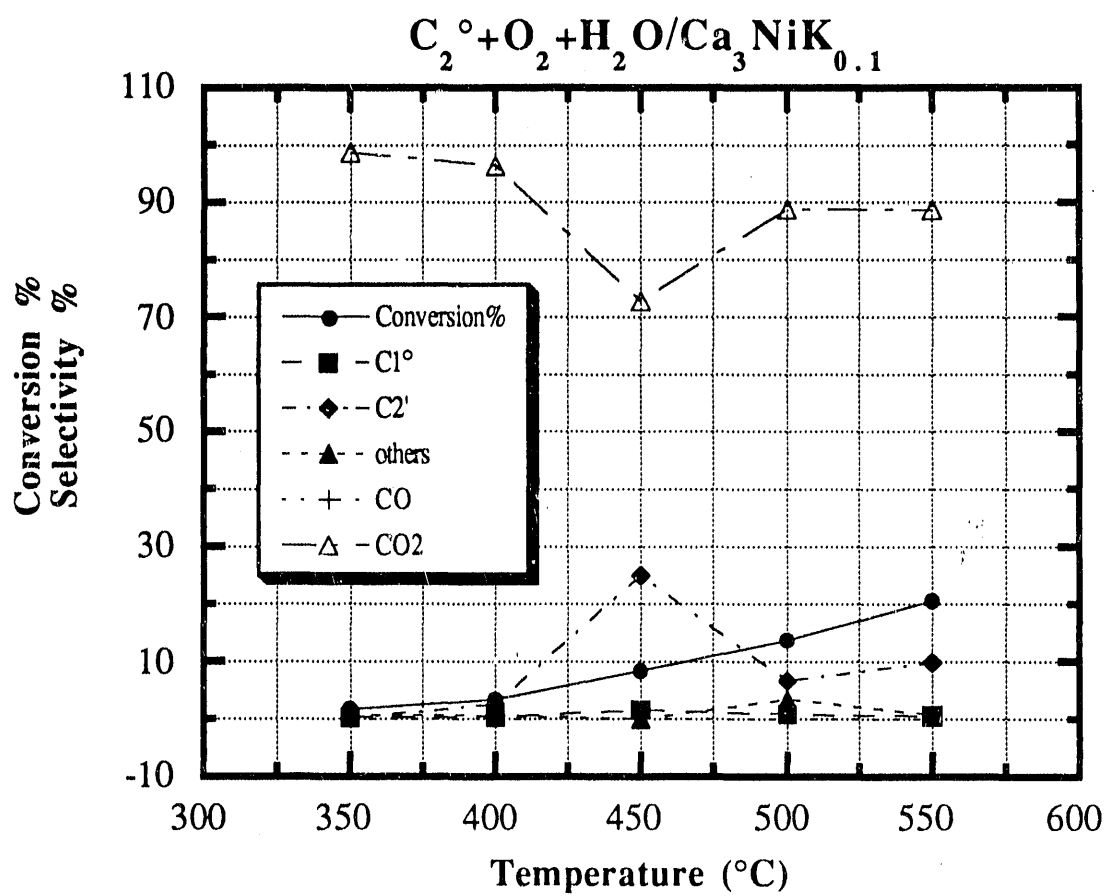


Figure 10

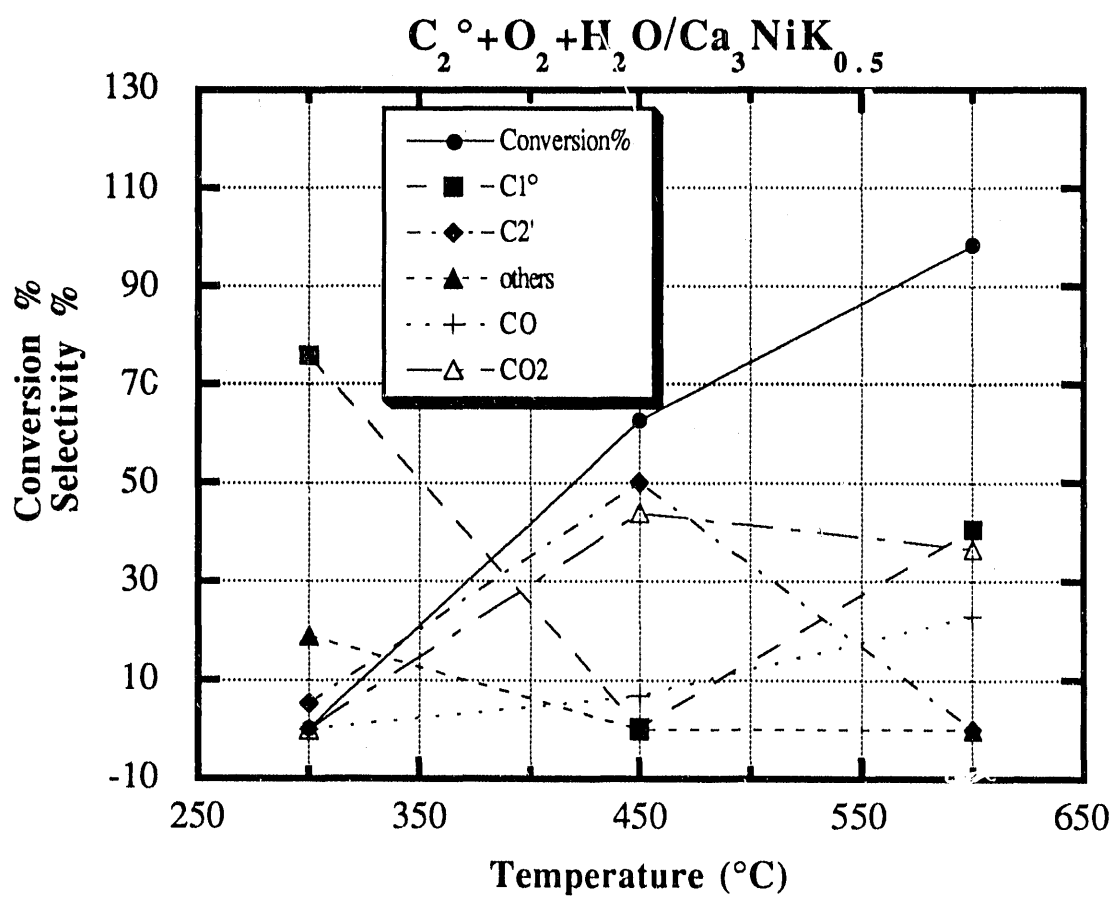


Figure 11

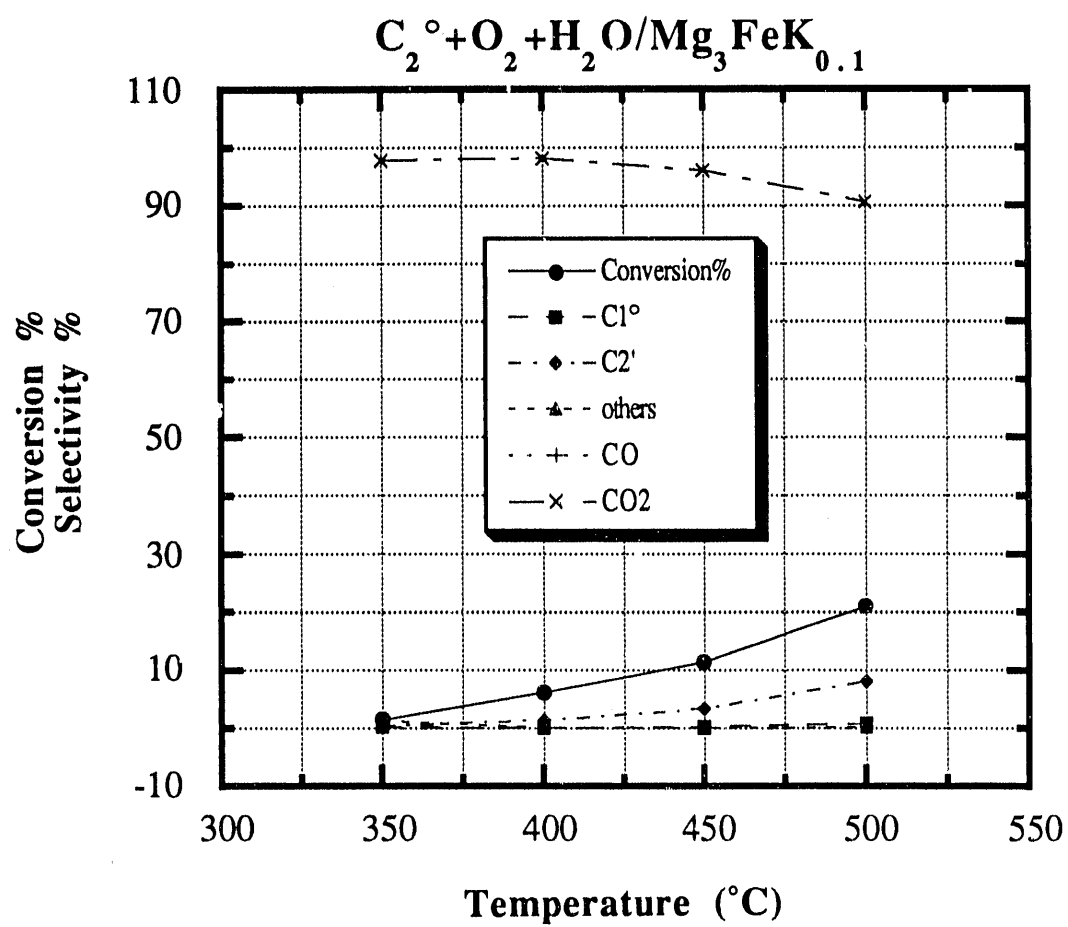


Figure 12

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