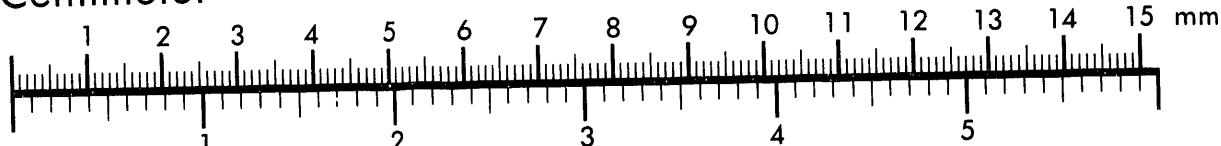




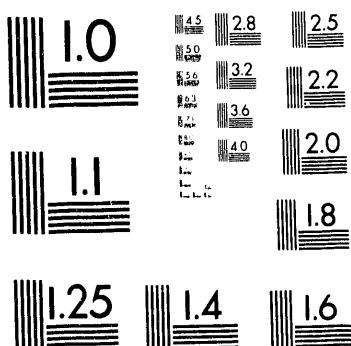
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**QUARTERLY REPORT**

April 1, 1992 - June 30, 1992

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

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## I. Task Description for FY 1997

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 CO<sub>2</sub> are formed at the higher temperatures and conversions are relatively low at the lower temperatures. However, there are indications that the objective of preparing C<sub>6</sub> to C<sub>12</sub> 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

Work during this quarter was slowed by equipment troubles and failures. Replacement of a faulty flow controller shut the unit down for a five week period.

Work reported in the April 1 quarterly report has been extended from ethane to propane feed.

## III. Highlights

- A series of binary catalysts for the oxydehydrogenation of ethane was prepared, characterized and tested. The catalysts were: Mo<sub>19</sub>Nb<sub>1</sub>O<sub>x</sub>; Mo<sub>4</sub>V<sub>1</sub>O<sub>x</sub>; and V<sub>5</sub>Nb<sub>1</sub>O<sub>x</sub>.
- The combination of molybdenum and vanadium is more active and selective than vanadium-niobium or molybdenum and niobium.
- The presence of niobium in catalysts, particularly in ternary catalysts serves to inhibit CO<sub>2</sub> formation.

- Propane oxydehydrogenation occurs at lower temperatures than ethane conversion over both binary and ternary catalysts. However, selectivity to propylene is lower than for ethylene from ethane.
- Propylene is completely converted to carbon oxides when charged to the catalyst in the absence of propane.
- Attempts failed to obtain higher hydrocarbons by oligemerizing propylene over acidic catalysts as it is formed.

#### IV. Progress of Studies

##### IV-1 Experimental

A series of binary oxide catalysts (MoV; VNb; MoNb) was prepared and tested for the oxydehydrogenation of ethane. The catalysts were prepared, characterized and tested as described below:

###### *(a) Catalyst Preparation*

The calculated amount (for example 10 mmol) of niobium pentachloride ( $\text{NbCl}_5$ , Johnson Matthey 99%) was hydrolysed in water (50 mL) and the turbid suspension was neutralized with ammonium hydroxide ( $\text{NH}_4\text{OH}$ , Aldrich). The white precipitate was filtered, washed with water and dissolved in a hot solution of oxalic acid dihydrate (50 mmol) ( $\text{HO}_2\text{CCO}_2\text{H} \cdot 2\text{H}_2\text{O}$ , Aldrich 99%). To this was added to an aqueous solution (50 mL) of ammonium metavanadate (50 mmol) at 90 °C, followed by an aqueous solution of ammonium paramolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , Johnson Matthey). The green slurry obtained was heated while stirring until the water was evaporated. The residue was dried for 16h at 120 °C, followed by the calcination in air at 400 °C for 4h. The powders obtained after that treatment were grey to dark blue. Similarly, catalysts comprising only 2 of the 3 metals were prepared using the same sequence and concentrations as described above.

To describe the composition of the catalysts, the following convention is used:  $\text{Mo}_\alpha\text{V}_\beta\text{Nb}_\delta\text{O}_x$ , where  $\alpha, \beta$  and  $\delta$  are the atomic proportions of the metals. For example, in  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  the Mo:V:Nb atomic ratio is 19:5:1.

(b) *Catalyst Characterization*

The surface areas (BET) were measured with a flow apparatus equipped with a thermal conductivity detector. The x-ray photoelectron spectra (XPS) were obtained using a Perkin-Elmer Phi 5300 ESCA instrument. The catalysts were pressed into a gold foil before the analysis. The error range for the atomic concentrations determined by XPS was estimated as 20%. The bulk analysis performed by atomic absorption on 3 different batches of  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  catalysts indicated Mo:V:Nb proportions of 7.3:1.3:1.0; 7.8:1.8:1.0 and 7.5:1.8:1.0.

(c) *Catalyst Testing*

The catalysts were tested under continuous flow conditions at atmospheric pressure. The tubular quartz reactor used had an inner diameter of 0.4 cm and a length of 20 cm. The reactor outlet was welded to a quartz capillary tube (1 mm I.D.) so that the products could be rapidly removed from the heated zone. The catalysts were packed on a thin layer of quartz wool. The void volume was minimized by the introduction a thermocouple covered with a 3 mm O.D. quartz tube in the center of the reactor. The temperature monitored at the top of the catalyst bed was controlled within  $\pm 1$  °C. The reagent gases (Matheson, CP grade) were mixed in the required amounts using mass flow controllers (Porter Instrument).

In the experiments, 0.50 g of catalysts were used with a total flow rate of 50 mL/min. The feed composition was ethane and oxygen in a ratio of 10:1, and propane, oxygen and helium in ratio of 10:3:87. In one experiment, 0.25 g of catalyst was mixed with 0.75 g of silica-alumina, which was activated at 300 °C for 12 hours. The studies were performed under atmospheric pressure at temperatures varying from 350 °C to 450 °C.

The products were analyzed by a gas chromatograph equipped with TCD detectors. Porapak Q (2 m, 25 °C) was used to separate  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$ . Molecular sieve 13X (2 m, 25 °C) was used to separate  $\text{O}_2$  and CO. Both columns were connected in series through a switching by-pass valve to isolate the MS-13X column while the  $\text{CO}_2$  and the hydrocarbons eluted from the Porapak column. The carbon balance was 100±5%.

#### IV-2 Ethane Conversion

Results of testing binary catalysts for the oxydehydrogenation of ethane should be compared with data for ternary catalysts presented in the April 1 report (LBL-32006), Tables 3, 4, 5, and 6.

To determine to what extent the simultaneous presence of the three oxides of molybdenum, vanadium and niobium is required and how they interact with each other, we prepared a series of catalysts composed of two of the three oxides (Table 1). The atomic proportions between any two

**Table 1.** Activity and selectivity of binary catalysts (0.50 g of catalysts,  $C_2H_6 : O_2 = 10 : 1$ , total flow rate: 50 mL/min)

Catalysts (surface area)	Temp. (°C)	Conversion (%)	Selectivity for		
			$C_2H_4$ (%)	CO (%)	$CO_2$ (%)
$Mo_4V_1O_x$ (10 m <sup>2</sup> /g)	390	1.1	78	20	2
	450	5.4	70	26	4
$Mo_4V_1O_x$ <sup>a)</sup> (7.5 m <sup>2</sup> /g)	390	1.7	79	16	5
	450	3.0	74	22	4
$V_5Nb_1O_x$ (22 m <sup>2</sup> /g)	390	3.0	43	52	5
	430	6.5	39	57	4
$Mo_{19}Nb_1O_x$ (11 m <sup>2</sup> /g)	390	0.5	91	9	-
	450	1.8	72	22	6

a) Catalyst prepared in the presence of 5 equivalents of oxalic acid

metals were held fixed relative to the proportions in  $Mo_{19}V_5Nb_1O_x$ . Each binary mixture was tested at 390 °C and 450 °C with 50 mL/min of ethane and oxygen in a 10:1 ratio. In the case of the  $Mo_4V_1O_x$  mixtures, one batch was prepared in the presence of five equivalents of oxalic acid. Although the ternary catalyst shows a 4%-5% ethane conversion at 390 °C, few binary mixtures reach 2% conversion. Only the  $V_5Nb_1O_x$  converts 3% of the ethane at that temperature. The  $Mo_{19}Nb_1O_x$  is the least active catalyst of the series with 0.5% of ethane conversion and 91% selectivity for ethylene at 390 °C., while at 450 °C, the conversion is 1.8% with 72% selectivity for ethylene. In the case of the  $Mo_4V_1O_x$ , the presence of five equivalents of oxalic acid during the catalyst preparation does not greatly affect the product distribution. At 390 °C, a conversion of

1.7% with 79% ethylene selectivity is obtained, while 1.1% of ethane is converted with 78% ethylene selectivity over the catalyst prepared without the oxalic acid. Although the most active mixture of the series, the  $V_5Nb_1O_x$  shows the worst selectivity. Only 43% of the ethane converted is converted to ethylene at 390 °C, while the carbon monoxide is the major product at 52% selectivity.

By comparing the catalytical activities and the ethylene selectivities between the binary catalysts and the  $Mo_6V_3Nb_1O_x$ ,  $Mo_8V_2Nb_1O_x$  or the  $Mo_{19}V_5Nb_1O_x$  (LBL-32006) it is obvious that the three components catalysts are much more active and selective than the binary catalysts. This is in agreement with Burch et al. (1) who observed a strong improvement in the efficiency from a  $Mo_6V_3O_x$  to a  $Mo_6V_3Nb_1O_x$  catalyst. Similarly, Thorsteinson et al. (2) found that the  $Mo_8V_2Nb_1O_x$  catalyzed the ethane oxidation exclusively to ethylene at 215 °C; whereas a temperature of 500 °C was necessary for the catalyst without niobium. Moreover the activity and selectivity depends on the ratio of the three components. The  $Mo_6V_3Nb_1O_x$  and the  $Mo_8V_2Nb_1O_x$  have approximately the same atomic content of niobium, but a molybdenum to vanadium ratio of 2:1 and 4:1, respectively. As it has been shown before, the  $Mo_8V_2Nb_1O_x$ , although less active, is more selective for the ethylene formation. By decreasing the niobium atomic ratio and keeping a Mo/V ratio of 4:1, the product distribution is not so severely altered: the ethylene selectivity is improved from 86% to 90% when the  $Mo_{19}V_5Nb_1O_x$  is used instead of the  $Mo_8V_2Nb_1O_x$ . Although the amount of niobium seems to be more flexible as compared to the other metals, a minimum is required. The  $Mo_{19}V_5Nb_{0.1}O_x$  has a comparable activity to the  $Mo_4V_1O_x$  catalysts. The superiority, in terms of selectivity, of a 4:1 ratio between the molybdenum and the vanadium is not particular to our experiments. Many examples can be found in the results published by Thorsteinson et al. (2).

The tests performed on the series of catalysts composed of two of the three metals show several interesting features: 1) the  $Mo_{19}Nb_1O_x$  is the poorest catalysts of the series; 2) the niobium in the vanadium oxide inhibits the total oxidation of ethane to carbon dioxide as compared to the pure vanadium pentoxide (3); 3) the  $Mo_4V_1O_x$  catalysts, with or without oxalic acid in their preparation, are still the most efficient in the series of the binary catalysts. These observations show that the combination of oxides of molybdenum and vanadium is already more active and selective than the vanadium-niobium or the molybdenum-niobium combinations. The intrinsic activity of the  $Mo_4V_1O_x$  is enhanced by the addition of niobium. An other major effect of this metal is emphasized by the results obtained with the  $V_5Nb_1O_x$  catalyst. In this catalyst, the presence of niobium inhibits the carbon dioxide formation to negligible quantities. The ethane oxidation over pure vanadium pentoxide has been reported to form considerable amounts of carbon dioxide and

carbon monoxide (3). This is also observed in the case of the  $\text{Mo}_{19}\text{V}_5\text{Nb}_{0.1}\text{O}_x$ . Although the quantity of niobium is not enough to have a significant effect on the activity, the rate of carbon dioxide formation is reduced by half as compared to the  $\text{Mo}_4\text{V}_1\text{O}_x$  catalyst prepared in the presence of oxalic acid.

According to these findings, it appears that the active phase of these catalysts is based on molybdenum and vanadium. The introduction of niobium considerably enhances the activity and improves the selectivity by inhibiting the total oxidation reaction. Taken together with earlier published results, our studies show that a 4:1 ratio between molybdenum and vanadium is optimum.

Our results suggest that the active phase of these catalysts is based on molybdenum and vanadium. The introduction of niobium enhances considerably the intrinsic activity of the molybdenum-vanadium combination. Moreover the niobium improves the selectivity for ethylene by inhibiting the total oxidation reaction. In the presence of niobium, a 4:1 atomic ratio between molybdenum and vanadium seems to be the optimum in terms of selectivity. The activation energies determined for the transformation of ethane to ethylene, carbon monoxide and dioxide on the  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  and the  $\text{MoV}_5\text{Nb}_1\text{O}_x$  are equivalent within the error range ( $\pm 2$  kcal/mol) and follow similar trends. Carbon monoxide formation is the most sensitive to temperature variation, which corresponds to  $E_a=31$  kcal/mol over  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  and  $E_a=27$  kcal/mol over  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$ . Carbon dioxide is the least sensitive with  $E_a=16$  kcal/mol and  $E_a=17$  kcal/mol, respectively. Ethylene formation has an intermediate position between CO and  $\text{CO}_2$  with  $E_a=20$  kcal/mol and  $E_a=18$  kcal/mol, respectively. This indicates that these products may be formed by parallel reactions. The stability with the time on stream of the  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$ ,  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  and the  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  were compared. The  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  deactivates rapidly at the beginning of a run. An increase of the amount of the carbon species on the surface may be the cause of the loss of activity.

#### IV-3 Propane Conversion

##### *(a) Temperature and Composition Dependence*

The conversion of propane and the product selectivities were determined in a temperature range of 350 °C to 450 °C and with a total flow rate of 50 mL/min. The inlet gas is composed of propane, oxygen and helium in a ratio of 10:3:87. Figures 1 to 4 display the temperature dependence of the propane conversion and the selectivities over the  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  ( $8.4 \text{ m}^2/\text{g}$ ),

$\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  ( $12 \text{ m}^2/\text{g}$ ),  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  ( $10 \text{ m}^2/\text{g}$ ) and the  $\text{Nb}_5\text{V}_1\text{O}_x$  ( $16 \text{ m}^2/\text{g}$ ) catalysts. The four catalysts show similar product selectivity variation with the conversion. For example, at a propane conversion of about 5%, a propylene selectivity of 47% is obtained over  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  at  $350^\circ\text{C}$ ; 52% over  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  at  $357^\circ\text{C}$ ; 50 % over  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  at  $357^\circ\text{C}$  and 47% over  $\text{Nb}_5\text{V}_1\text{O}_x$  at  $450^\circ\text{C}$ . However, the  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  catalyst is the most active and the  $\text{Nb}_5\text{V}_1\text{O}_x$  catalyst the least active for the propane oxidehydrogenation.

(b) *Propane and Propylene Reactivity*

The conversion and the product selectivities obtained with propane and propylene are compared at  $390^\circ\text{C}$  over the  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  catalyst (Table 2). Only 7.0% of propylene are converted to carbon monoxide and carbon dioxide, whereas 12% of propane are converted to propylene, carbon monoxide and carbon dioxide.

**Table 2.** Comparison of the reactivities of propane and propylene over  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  (0.50 g of catalysts,  $390^\circ\text{C}$ , total flow rate: 50 mL/min)

Feed composition (ratios)	Conversion (%)	Selectivity for		
		$\text{C}_3\text{H}_6$ (%)	CO (%)	$\text{CO}_2$ (%)
$\text{C}_3\text{H}_8:\text{O}_2:\text{He}$ (10 : 3 : 87)	12	29	49	23
$\text{C}_3\text{H}_6:\text{O}_2:\text{He}$ (10 : 3 : 87)	7.0	-	43	57
$\text{C}_3\text{H}_6:\text{O}_2:\text{He}$ (1.7 : 3 : 95.3)	57	-	55	45

(c) *Effect of An Acidic Catalyst*

The goal is to allow propylene to form oligomers, perhaps eventually some aromatics, by adding an acidic catalyst to the molybdenum, vanadium, niobium oxides mixture. Therefore

$\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  was mixed with activated silica-alumina and the reaction was run at 390 °C. In order to trap high molecular weight products, the condenser at the outlet of the reactor was immersed in a bath at about -40 °C. As shown in Table 3, at a conversion of propane of 6-6.5%, the propylene selectivity is 38% at 390 °C. No higher hydrocarbons were found.

**Table 3.** Reaction of propane over a mixture of 0.25 g of  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  and 0.75 g of silica-alumina (0.50 g of catalysts, 390 °C, total flow rate: 50 mL/min)

Time on stream (min)	Conversion (%)	Selectivity for		
		$\text{C}_3\text{H}_6$ (%)	CO (%)	$\text{CO}_2$ (%)
30	6.5	38	37	25
2900	6.2	39	38	23

Just as in the oxydehydrogenation of ethane over the three component catalysts, the greatest difference in catalysts performance is observed between the  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  and the  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  and the  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  catalysts. The last two display a propylene selectivity of about 30%-35% at 10% propane conversion at 390 °C. The  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$ , the more active of the series, show 28% propylene selectivity at a conversion of 12% at 390 °C. The binary catalyst  $\text{Nb}_5\text{V}_1\text{O}_x$  needs much higher temperatures to compete with the ternary catalysts.

Because of its high conversion of propane,  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  was chosen to compare the reactivity of propylene relatively to propane. The aim of that experiment was to determine to what extent the propylene formed during oxydehydrogenation of propane is further oxidized to carbon monoxide and carbon dioxide. Comparison of the conversions of propane and of propylene over  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  at 390 °C indicates that the carbon oxides formed during the propane oxydehydrogenation are essentially derived from the alkane conversion.

The  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  was mixed with silica-alumina in order to provide the acidic partner necessary for oligomerization of propylene. The idea is to take advantage of the temperature range of 350-450 °C of the molybdenum, vanadium, niobium oxides catalysts, at which propylene can

be converted over acidic catalysts. However the addition of silica-alumina does not lead to the formation of higher hydrocarbons at our experimental conditions. Moreover, with a conversion of propane of 6-6.5%, the product distribution is similar as compared to the selectivities obtained with pure  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  at the same conversion of propane (Table 3 and Figure 3). These results indicates that the addition of silica-alumina does not have any effect. Although the reaction is run at 390 °C, the water formation may poisonned the hydrophilic silica-alumina.

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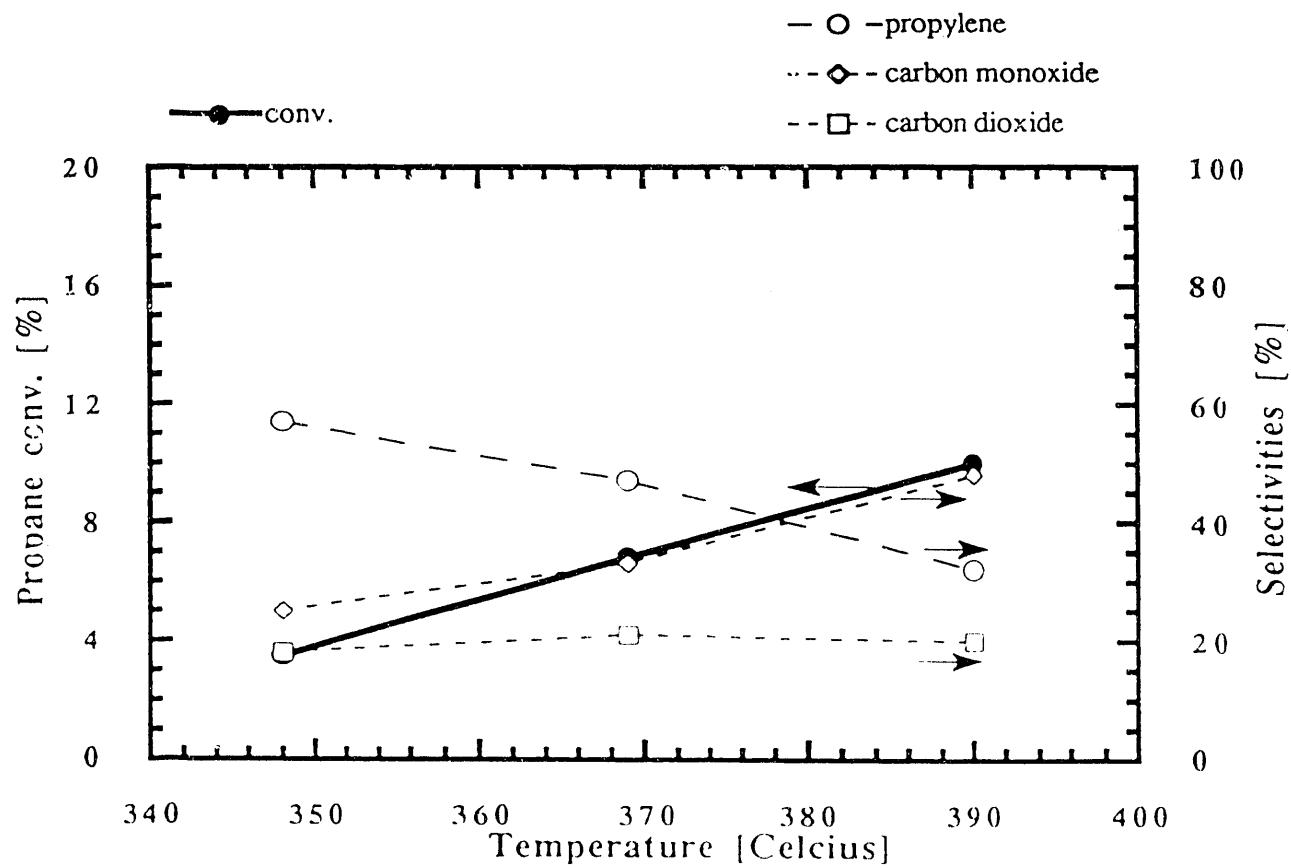


Figure 1. Propane conversion and products selectivities as a function of the temperature over  $\text{Mo}_{19}\text{V}_5\text{Nb}_1\text{O}_x$  ((0.50 g of catalysts,  $\text{C}_3\text{H}_8:\text{O}_2:\text{He} = 10:3:87$ , total flow rate: 50 mL/min).

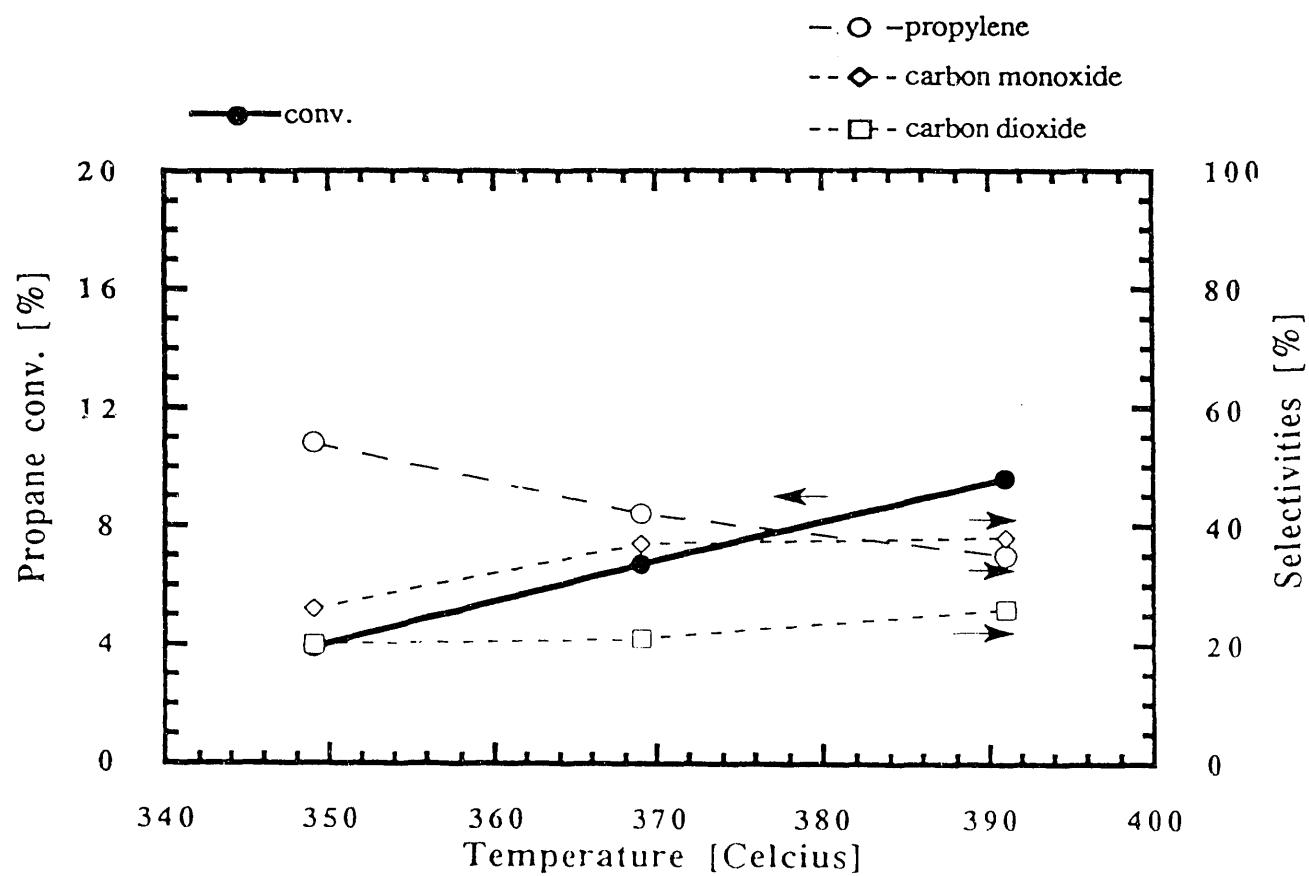


Figure 2. Propane conversion and products selectivities as a function of the temperature over  $\text{Mo}_8\text{V}_2\text{Nb}_1\text{O}_x$  (0.50 g of catalysts,  $\text{C}_3\text{H}_8:\text{O}_2:\text{He} = 10:3:87$ , total flow rate: 50 mL/min).

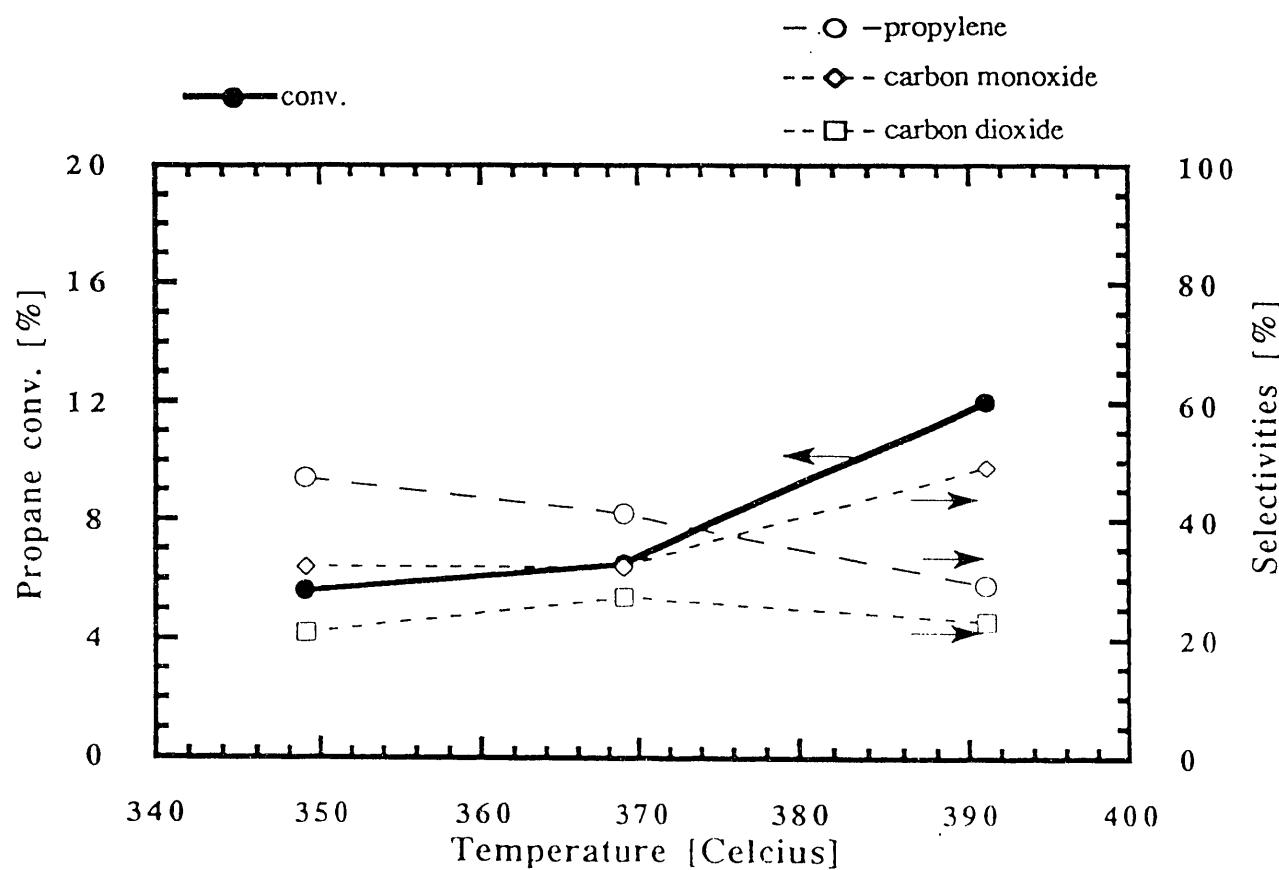


Figure 3. Propane conversion and products selectivities as a function of the temperature over  $\text{Mo}_6\text{V}_3\text{Nb}_1\text{O}_x$  (0.50 g of catalysts,  $\text{C}_3\text{H}_8:\text{O}_2:\text{He} = 10:3:87$ , total flow rate: 50 mL/min).

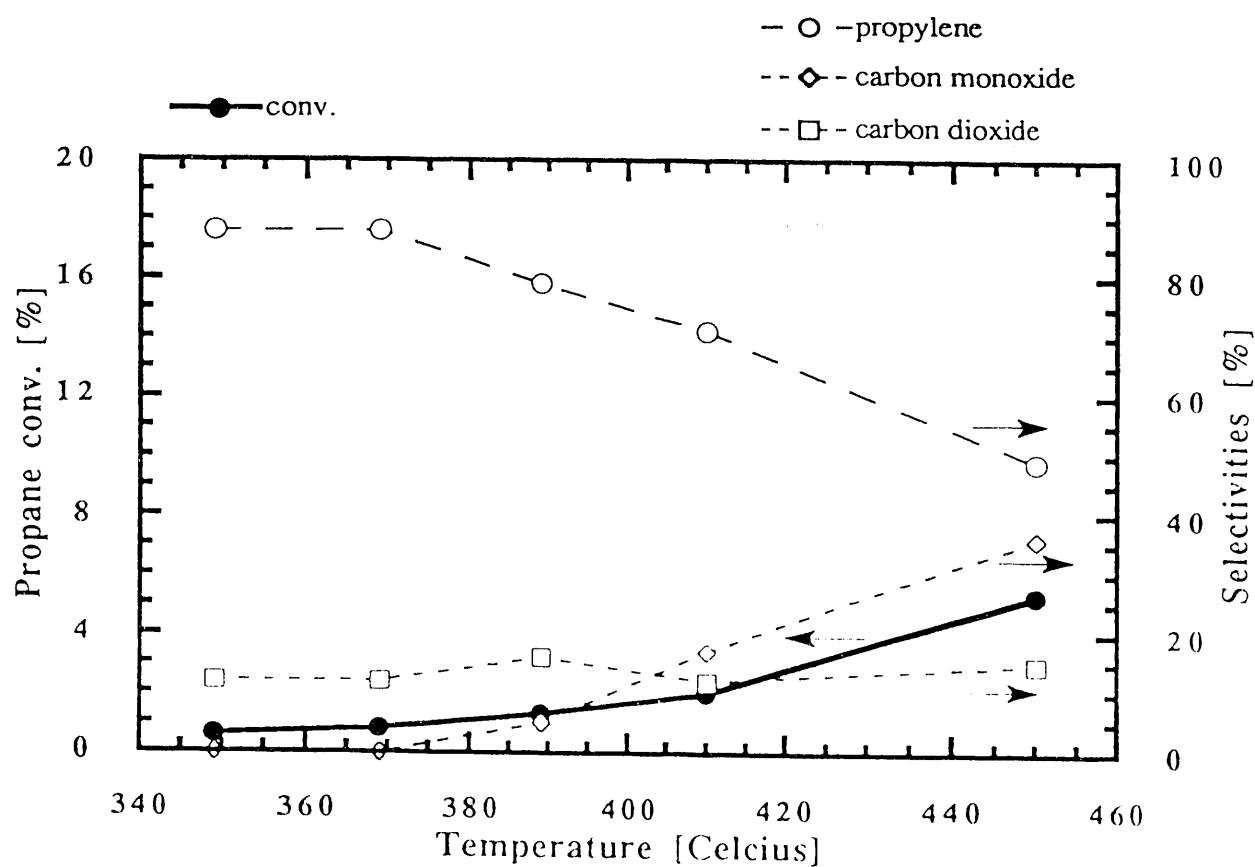


Figure 4. Propane conversion and products selectivities as a function of the temperature over  $\text{Nb}_5\text{V}_1\text{O}_x$  (0.50 g of catalyst,  $\text{C}_3\text{H}_8:\text{O}_2:\text{He} = 10:3:87$ , total flow rate: 50 mL/min).

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