PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY. PROGRESS REPORT, APRIL 1, 1982-MARCH 31, 1983

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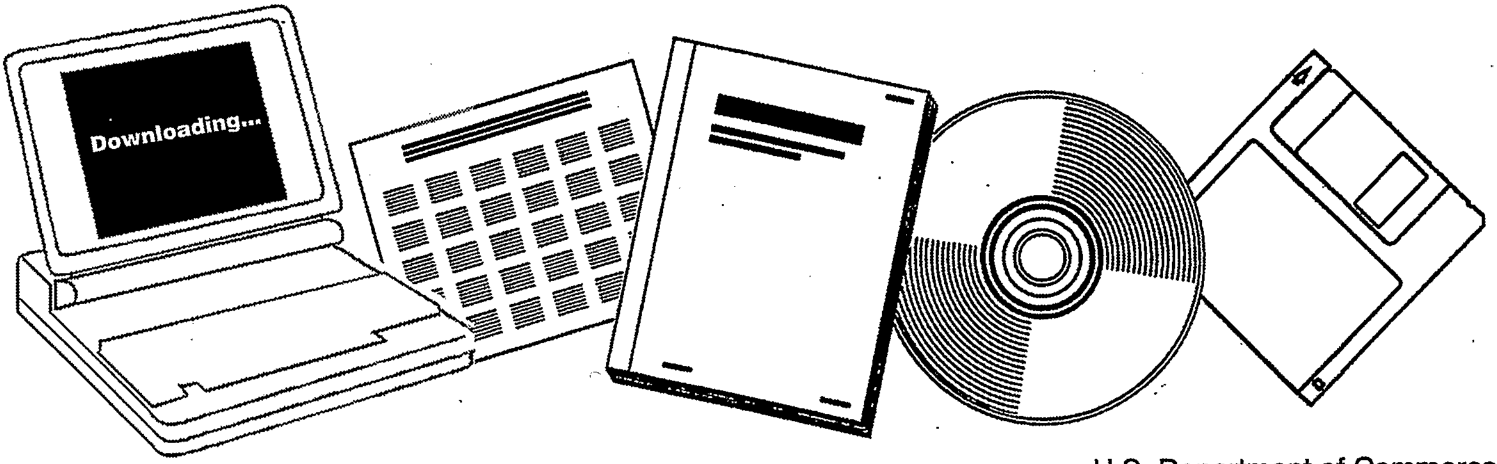

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"PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY"

Progress Report

for Period April 1, 1982-March 31, 1983

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NOTICE

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Abstract

The influence of alkali promoters on CO hydrogenation was studied as a function of catalyst support (Al_2O_3, SiO_2, $SiO_2 \cdot Al_2O_3$ and TiO_2). Temperature-programmed reaction was used to study the specific rates of CO and carbon hydrogenation, and temperature-programmed desorption studied the change in H_2 and CO desorption rates. The role of the support was separately studied for comparison. Specific activity and product distributions were also studied in a differential reactor with gas-chromatography detection. On all catalysts the selectivity for higher hydrocarbons, particularly olefins, was increased by addition of Na or K promoters. On all catalysts but $Ni/SiO_2 \cdot Al_2O_3$, however, the specific activity decreased; on $Ni/SiO_2 \cdot Al_2O_3$, a slight increase in specific activity was seen. Similarly, significant changes in methanation activation energies were observed for the addition of promoters. Good agreement was obtained between differential reactor studies and temperature-programmed reaction. The role of the promoter is significantly influenced by the oxide support.

Introduction

A typical supported-metal catalyst contains one or more noncatalytic promoters, often alkali metals, that change the activity and selectivity. The effect of those promoters appears to depend on the support and the method of preparation. This research is aimed at understanding how the catalytically-inert alkali metal changes activity and selectivity. Carbon monoxide hydrogenation is being studied on supported nickel and ruthenium.

Temperature-programmed desorption (TPD) and reaction (TPR) are being used with mass spectrometric detection to determine how promoters affect binding energies, individual reaction steps, reaction mechanism and catalytic activity. Differential reactor kinetic studies with gas chromatographic analysis is used to measure selectivity and activity. X-ray photoelectron spectroscopy will be used to determine the concentration and chemical state of the promoter.

Project Status, Accomplishments and Technical Discussion

Temperature-programmed desorption (TPD) and reaction (TPR) and differential reactor kinetic studies were applied to a number of catalysts prepared in our laboratory. These catalysts were prepared by impregnation procedures with various concentrations of sodium and potassium promoters. The alkali salts were used as the promoter source. Unpromoted catalysts were also prepared. The weight loadings were measured, for both nickel and the alkali, by atomic absorption. Some of the catalysts were also characterized by Auger spectroscopy and x-ray photoelectron spectroscopy to verify the presence of the alkali at the surface.

We will present results mainly for TPR and differential reactor studies. Both the influence of promoters and supports and the effects of support on the promoter were studied. In a few cases, the effect of promoter concentration was also measured.

a normal TPR. Using computer switching between mass peaks, methane (mass 15), ethane (mass 30), propane (mass 43) and mass 44 (propane and carbon dioxide) were simultaneously monitored as a function of temperature. Figures 1-4 show the reaction products for seven different initial coverages. Table 1 shows the interruption temperature used for the data and the fraction of saturation coverage of methane.

Methane and ethane were formed in narrow peaks and two distinct methane peaks were seen. Ethane formed at a slightly lower temperature than methane; the ethane yield was only one-hundredth of the methane. The methane, ethane and propane peak temperatures did not change with initial coverage, indicating first-order processes for all three products. Masses 43 and 44 were used to identify propane. Since mass 44 was broader than 43, it probably has a contribution from CO_2 and from propane. Olefins are not expected to form in TPR experiments because of the large excess of H_2. Also, ethylene would be difficult to detect because of desorption of unreacted CO.

Even for the high H_2:CO ratio that is present during TPR, the Ni/TiO_2 catalyst still forms ethane and propane. Though these quantities are small, they are detectable with the mass spectrometer system and the results in Figure 1-4 show the ability of TPR to study catalytic reactions with high senstivity.

Promoters: The influence of alkali promoters has been studied on Ni/SiO_2, $Ni/SiO_2 \cdot Al_2O_3$ and Ni/TiO_2 with temperature-programmed desorption (TPR). By using TPR, specific rates of reaction to methane and ethane were measured, independent of surface area measurements. The effect of promoter concentration was also studied. On Ni/SiO_2, sodium and potassium were found to significantly decrease the rate of CO hydrogenation to both methane and ethane (see Figure 5). Similarly, on Ni/TiO_2, potassium decreased the specific rate of hydrogenation. Similar decreases have been seen in the steady-state hydrocarbons and activities were measured in agreement with those reported in the literature. Catalytic activities and selectivities were then compared for catalysts on various supports, with and without promoters. As shown in Table 3, for similar weight loadings, the activity per gram of nickel was highest for Ni/TiO_2, as expected from reports in the literature. The turnover numbers have not yet been determined. These data are for a 3:1 ratio of H_2:CO and for conversions below five percent.

The most important observation from these data is that on Ni/SiO_2 and Ni/TiO_2, the methanation activity decreased significantly with the addition of 1% K. On Ni/SiO_2, the activity also decreased for 0.9% Na promoter, though the decrease was not as large as for potassium. In contrast, the activity for $Ni/SiO_2 \cdot Al_2O_3$ was essentially the same. That is, the change in the activity is dramatically dependent on the support used. This is in agreement with the temperature-programmed reaction results, which show that the alkali promoters cause a decrease in specific activity for Ni/SiO_2 and Ni/TiO_2 and an increase for $Ni/SiO_2 \cdot Al_2O_3$. This shows the values of TPR for rapid characterization of catalysts.

Table 4 shows the apparent activation energies measured for the same catalysts. On Ni/SiO_2 and $Ni/SiO_2 \cdot Al_2O_3$, promoters increase the activation energy, with a particularly large increase seen for Ni/SiO_2. On Ni/TiO_2, a slight decrease was seen in activation energy. In Tables 3 and 4 the reduction temperature was varied between 450 and 550°C to observe possible effects of strong metal-support interactions. On unpromoted Ni/TiO_2, the activity decreased while on promoted Ni/TiO_2, a slight increase in activity was seen. Similarly, the activation energy increased slightly with higher reduction temperature.

Figures 7-12 present the product distributions, as a function of temperature, for the promoted and unpromoted catalysts on these three supports. As

A small effect due to increased reduction temperature was observed for the Ni/TiO_2 catalysts; no dramatic changes were seen. Most of the data for Ni/TiO_2 were for reduction at 450°C.

Conclusions

Carbon monoxide hydrogenation to methane and higher hydrocarbons was studied with temperature-programmed reaction and with a differential reactor. Alkali promoters significantly change activity and selectivity on nickel catalysts. The support also independently affects selectivity and the influence of the alkali promoter depends significantly on the support.

For all supports studied (SiO_2, TiO_2, $SiO_2 \cdot Al_2O_3$), sodium and potassium promoters increase the selectivity towards higher hydrocarbons, particularly towards olefins. For Ni/SiO_2, for example, a factor of thirty increase in ethylene percentage was seen. However, with the exception of silica·alumina-supported nickel, the overall rate of reaction is significantly decreased by alkali. On $Ni/SiO_2 \cdot Al_2O_3$, the activity increases. Temperature-programmed reaction also shows that both carbon and carbon monoxide hydrogenation rates are decreased on Ni/SiO_2, apparently due to decreased bonding of hydrogen. Agreement in these studies between TPR and steady-state kinetics is excellent.

Preprints

"CO Methanation on Low Weight-Loading Ni/Al_2O_3: Multiple Reaction Sites," by K. B. Kester and J. L. Falconer, submitted to J. Catalysis (preprint attached).

"Alkali Promoters on Nickel: Influence of Catalyst Support on Methanation," by J. L. Falconer and P. D. Gochis, to be submitted to J. Catalysis (preprint will be forwarded to DOE).

Table 1

10% Ni/TiO_2: Temperature-Programmed Reaction

Curve	Interruption Temperature (K)	Methane Coverage (%)
a	300	100
b	395	97.4
c	407	91.6
d	416	77.6
e	425	52.4
f	430	36.0
g	434	17.8

Table 2

Peak Temperatures from TPR Carbon Monoxide

Catalyst	CH_4	C_2H_6	C_3H_8
Ni/SiO_2			
unpromoted	484	461	484
0.5% Na*	493	472	475
0.5% Na	514	500	497
0.6% K	521	488	497
0.9% K	550	498	447
$Ni/SiO_2 \cdot Al_2O_3$			
unpromoted	471	444	--
0.2% Na	465	445	442
0.3% Na	460,519	432	455

Table 3

Activity for CH_4 Formation at 548 K

$\left(\frac{\mu mole}{s \cdot gNi}\right)$

Catalyst	--	1% K	0.9% Na
10% Ni/SiO_2	135	1.36	11.3
10% Ni/$SiO_2 \cdot Al_2O_3$	99.6	103	--
10% Ni/TiO_2			--
Reduced 450	255	4.72	--
Reduced 500	218	5.65	--
Reduced 550	167	--	--

Table 4

Apparent Activation Energy for CH_4 Formation

(kJ/mol)

Catalyst	--	1% K	0.9% Na
10% Ni/SiO_2	103	145	106
10% $Ni/SiO_2 \cdot Al_2O_3$	110	125	--
10% Ni/TiO_2			
Reduced 450°C	129	125	--
Reduced 500°C	133	122	--
Reduced 550°C	136	--	--

Figure Captions

Figure 1	Methane TPR spectra for CO adsorbed on 10% Ni/TiO_2. Initial coverage was varied by interrupted reaction (see Table 1).
Figure 2	Ethane TPR spectra for CO adsorbed on 10% Ni/TiO_2 (see Table 1).
Figure 3	Propane TPR spectra (mass 43) for CO adsorbed on 10% Ni/TiO_2 (see Table 1).
Figure 4	Mass 44 TPR spectra (CO_2 and propane) for CO adsorbed on 10% Ni/TiO_2 (see table 1).
Figure 5	Hydrocarbon products for TPR of CO from Ni/TiO_2 (a) CH_4 (b) C_2H_6 and from 0.9% K on Ni/SiO_2 (c) CH_4 (d) C_2H_6
Figure 6	Hydrogen desorption spectra for hydrogen adsorption at 298 K on (a) 10.1% Ni/SiO_2 (b) 12.1% Ni/SiO_2 with 0.9% K promoter.
Figure 7	10% Ni/SiO_2 product distribution.
Figure 8	10% Ni/1% K/SiO_2 product distribution.
Figure 9	10% $Ni/SiO_2 \cdot Al_2O_3$ product distribution.
Figure 10	10% Ni/1% $K/SiO_2 \cdot Al_2O_3$ product distribution.
Figure 11	10% Ni/TiO_2 product distribution.
Figure 12	10% Ni/1% K/TiO_2 product distribution.

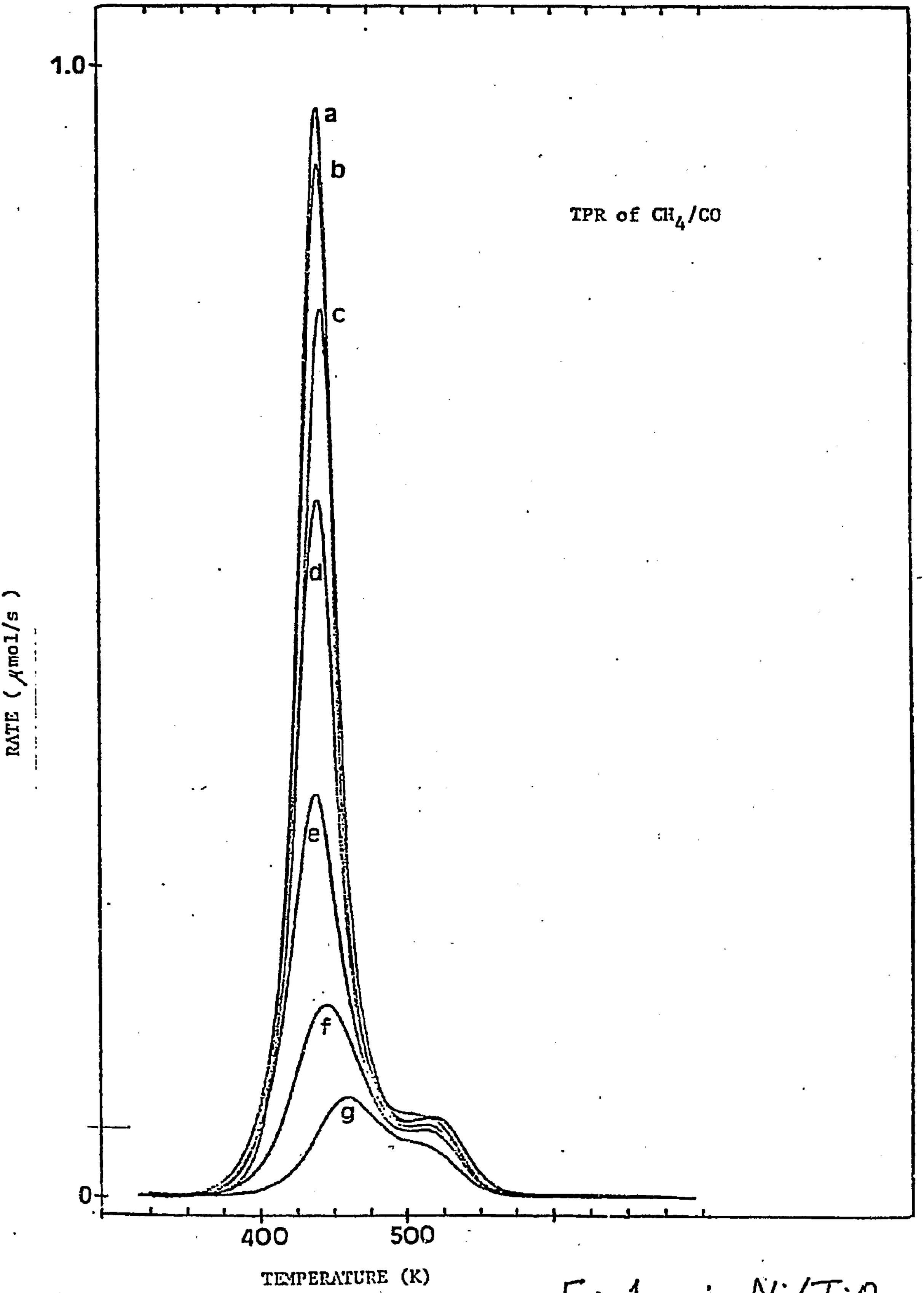

Fig 1 : Ni/TiO_2

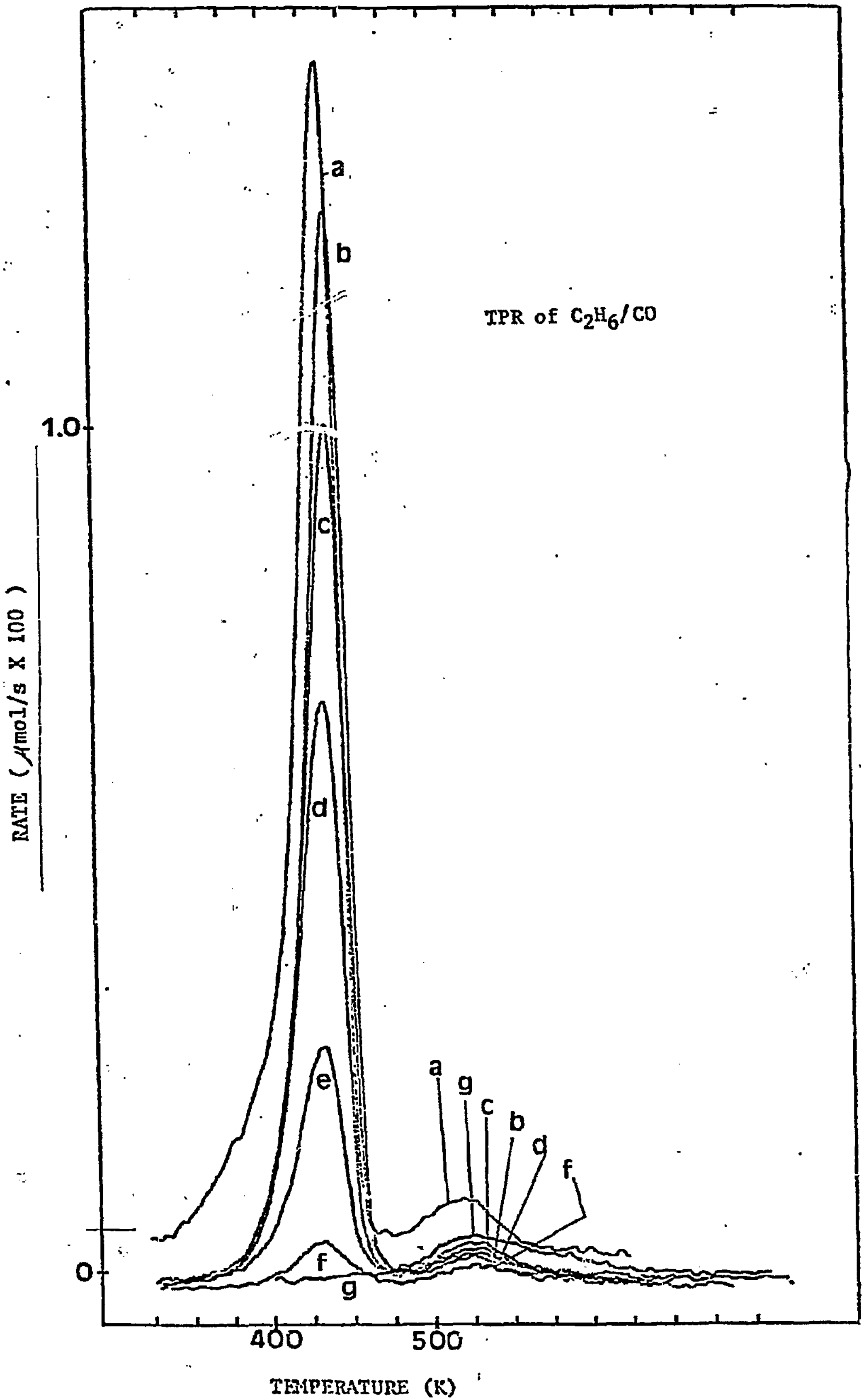
TPR of C_2H_6/CO
RATE (μmol/s X 100)
1.0
0
400
500
TEMPERATURE (K)
a
b
c
d
e
f
g
a
g
c
b
d
f

Fig 2 : Ni/TiO₂

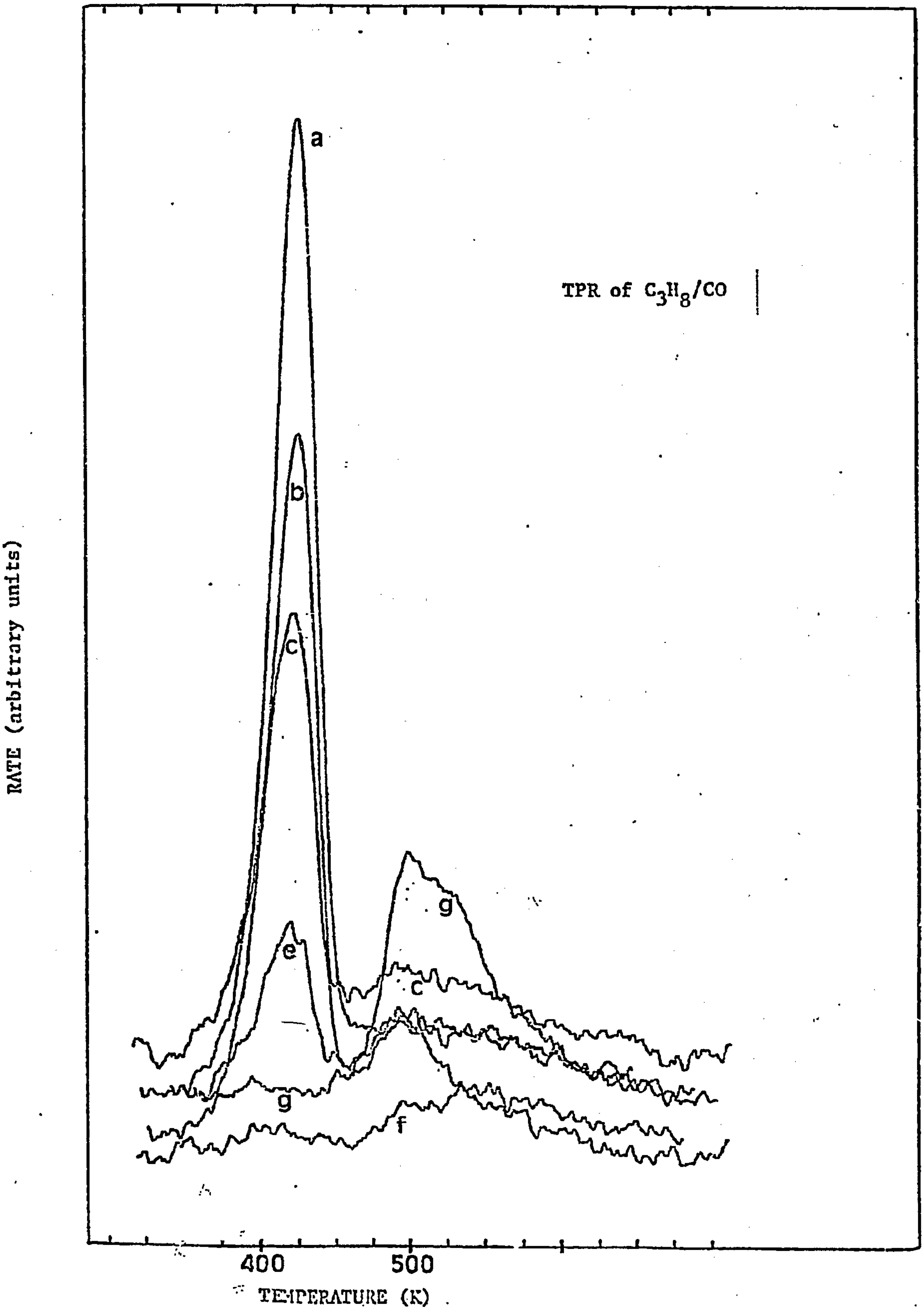
TPR of C_3H_8/CO
RATE (arbitrary units)
TEMPERATURE (K)
400
500
a
b
c
e
g
c
g
f

Fig 3 : Ni/TiO₂

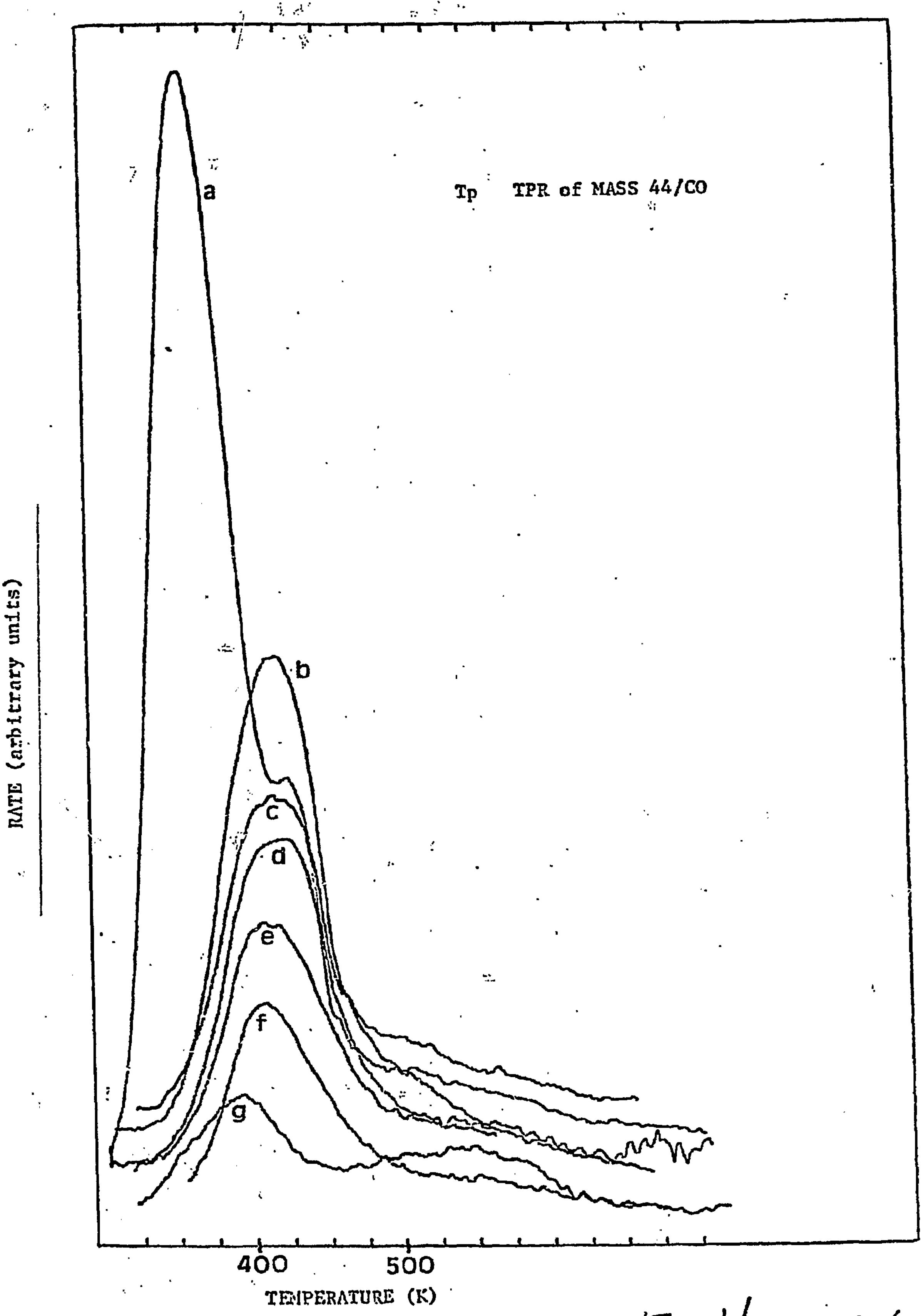
Tp
TPR of MASS 44/CO
a
b
c
d
e
f
g
RATE (arbitrary units)
400
500
TEMPERATURE (K)

Fig 4 : Ni/TiO2

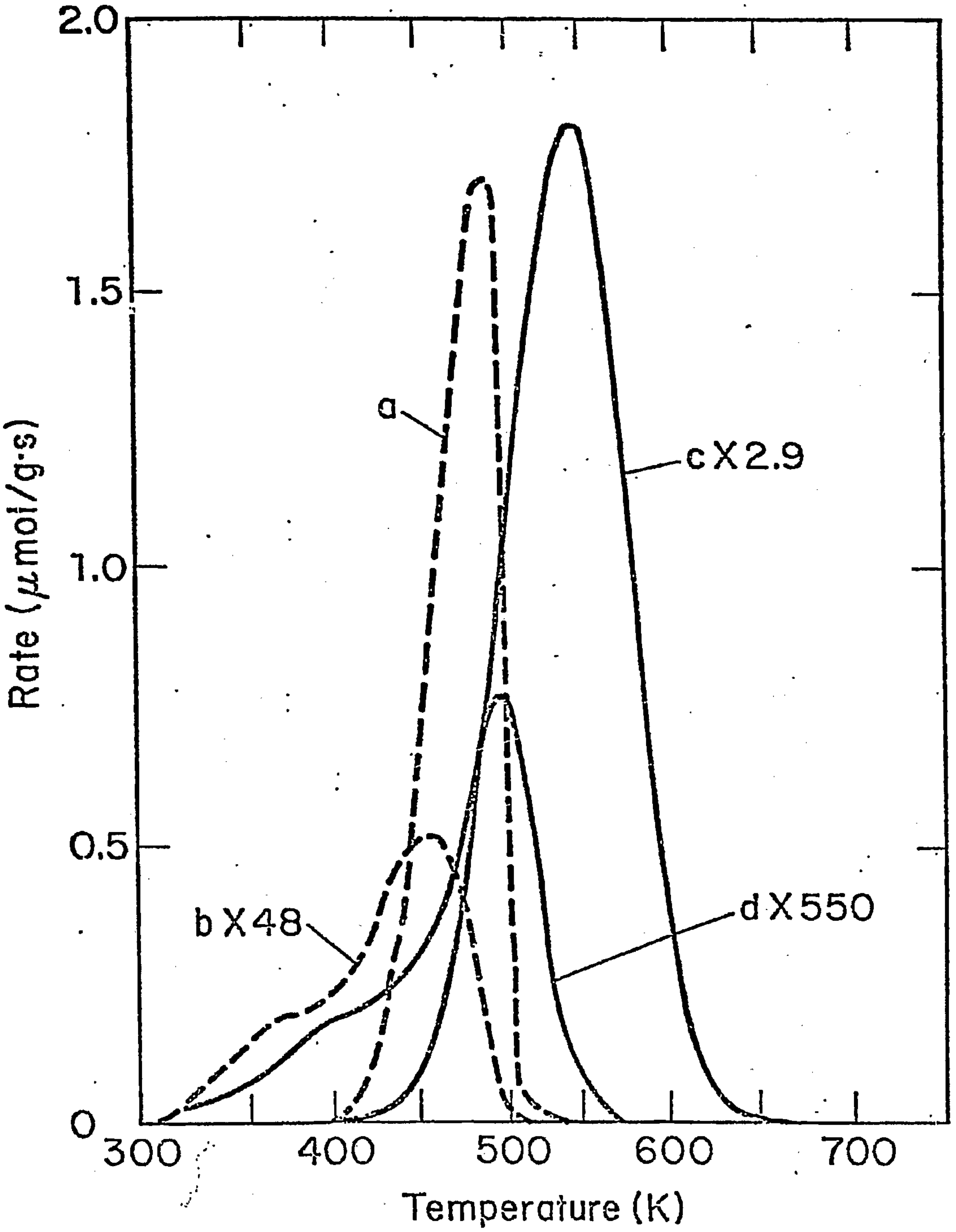
2.0
1.5
1.0
0.5
0
300
400
500
600
700
Rate (μmol/g·s)
Temperature (K)
a
b X48
c X2.9
d X550

Fig 5

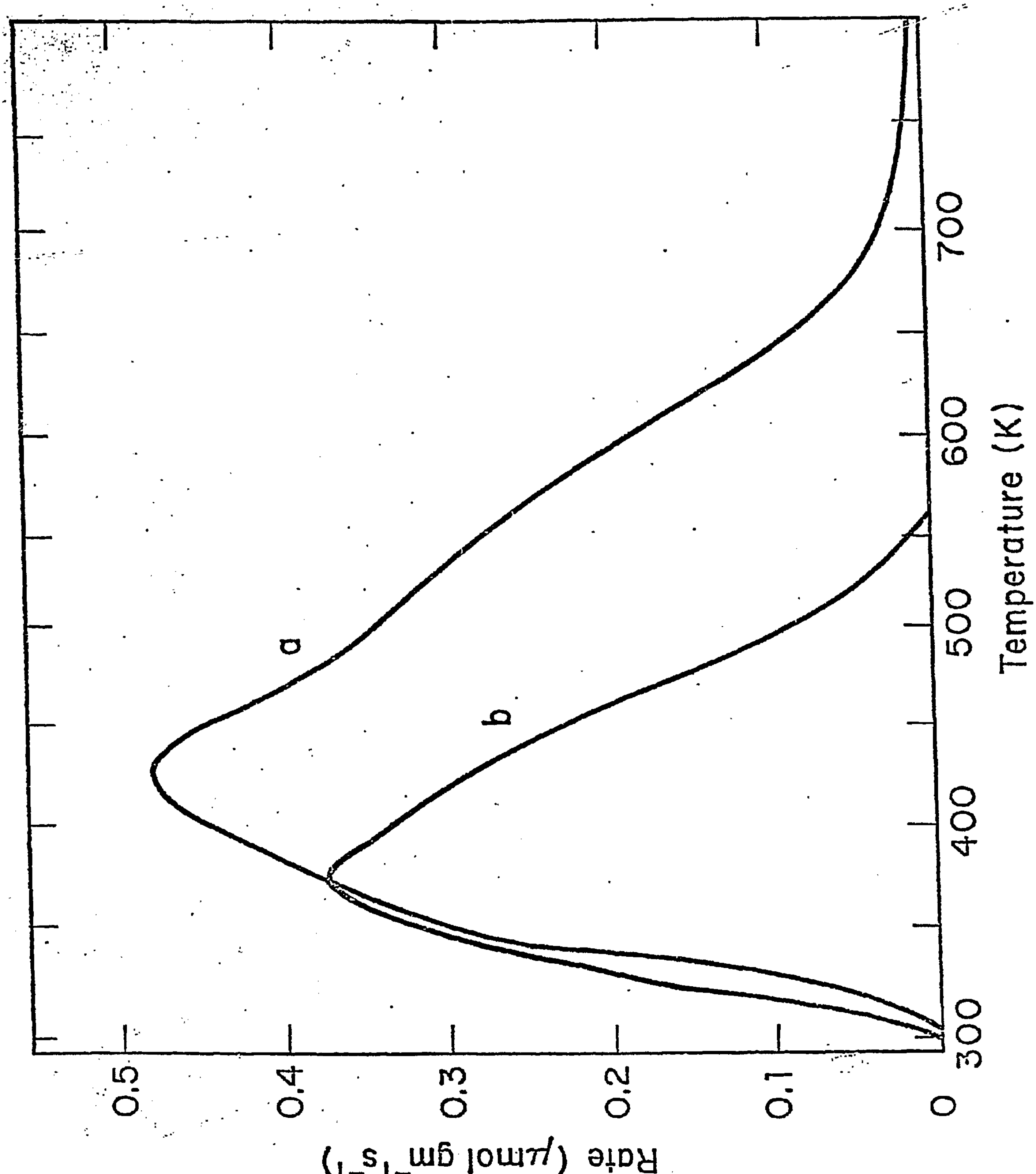
Rate (μmol gm^{-1}s^{-1})
0
0.1
0.2
0.3
0.4
0.5
Temperature (K)
300
400
500
600
700
a
b

Fig 6

10% Ni/SiO2 (without Promoter)

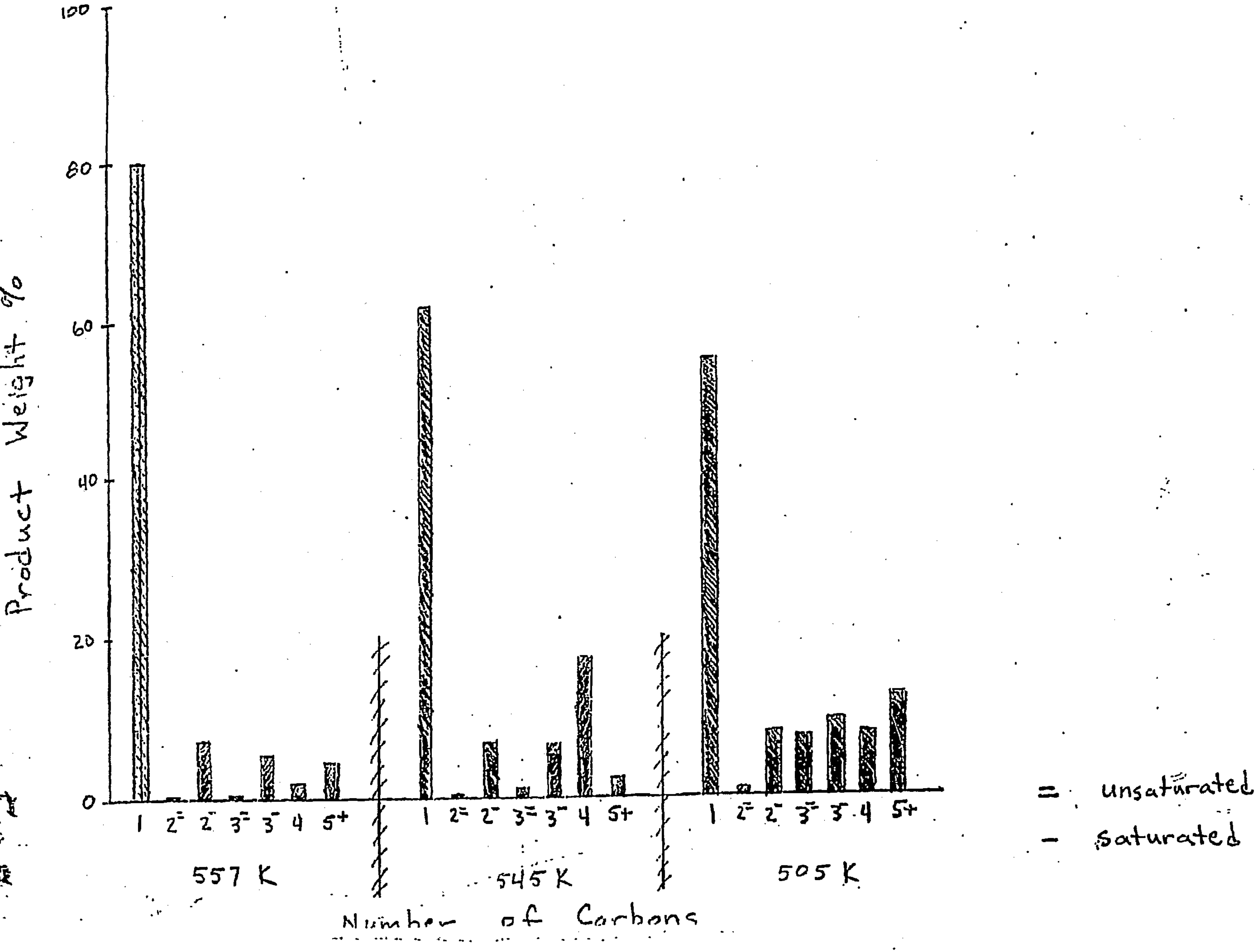

Fig 4

10%Ni/1%K/SiO2 (with promoter)

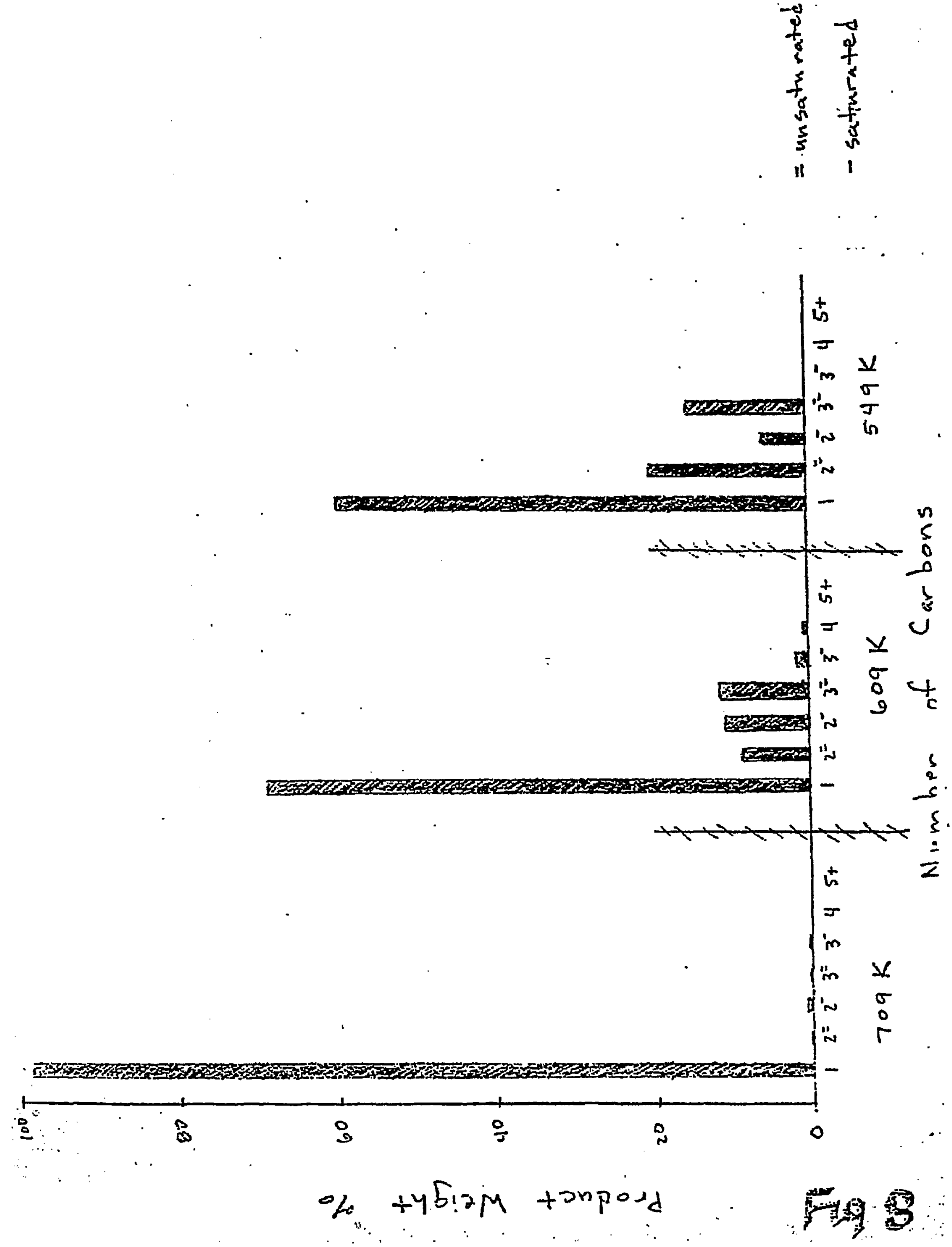

Fig 8

10% Ni/$SiO_2 \cdot Al_2O_3$ (without promoter)

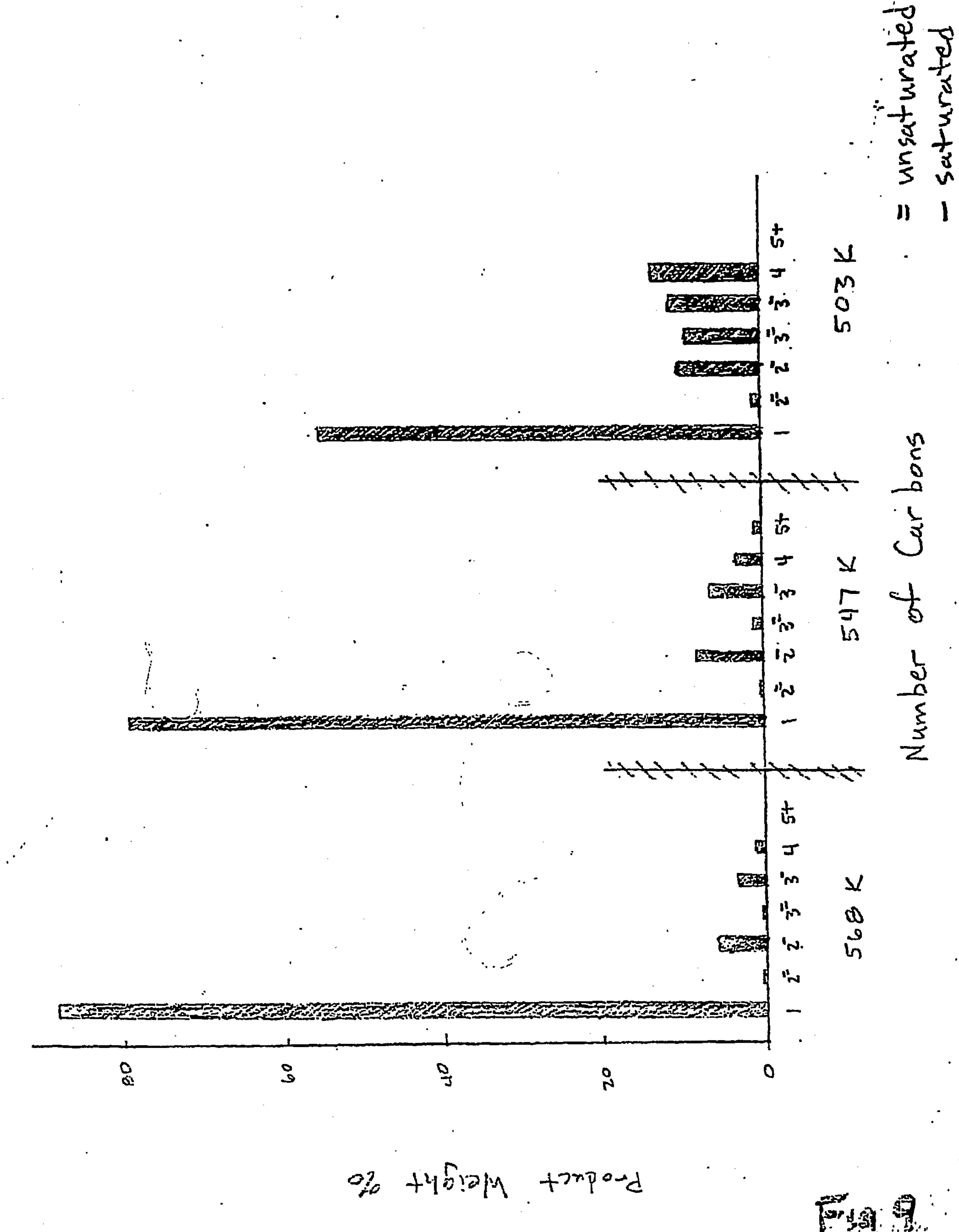

Fig. 9

10% Ni / 1% K / $SiO_2 \cdot Al_2O_3$ (with promoter)

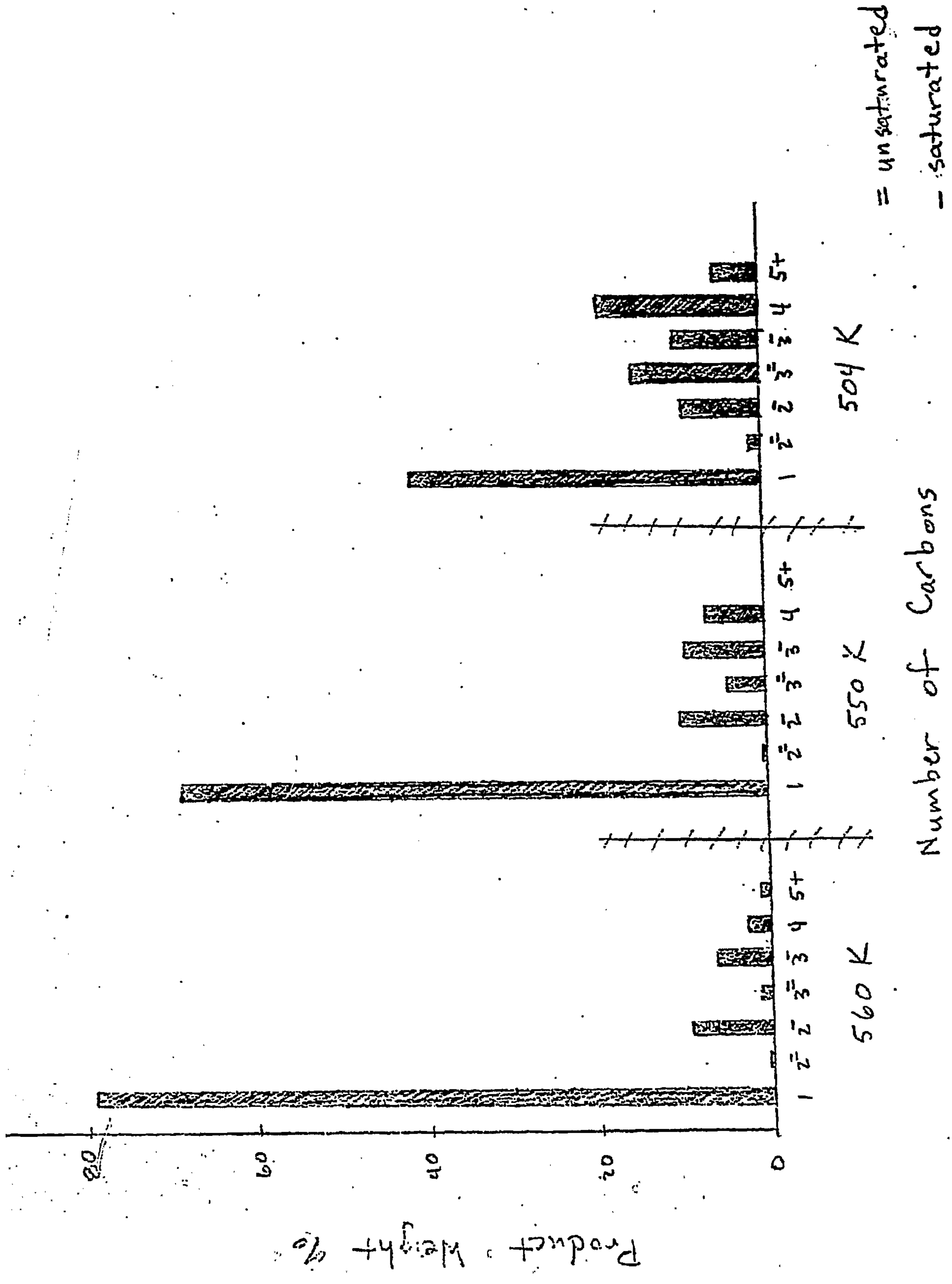

Fig 10

10% Ni/TiO2 (without Promoter)

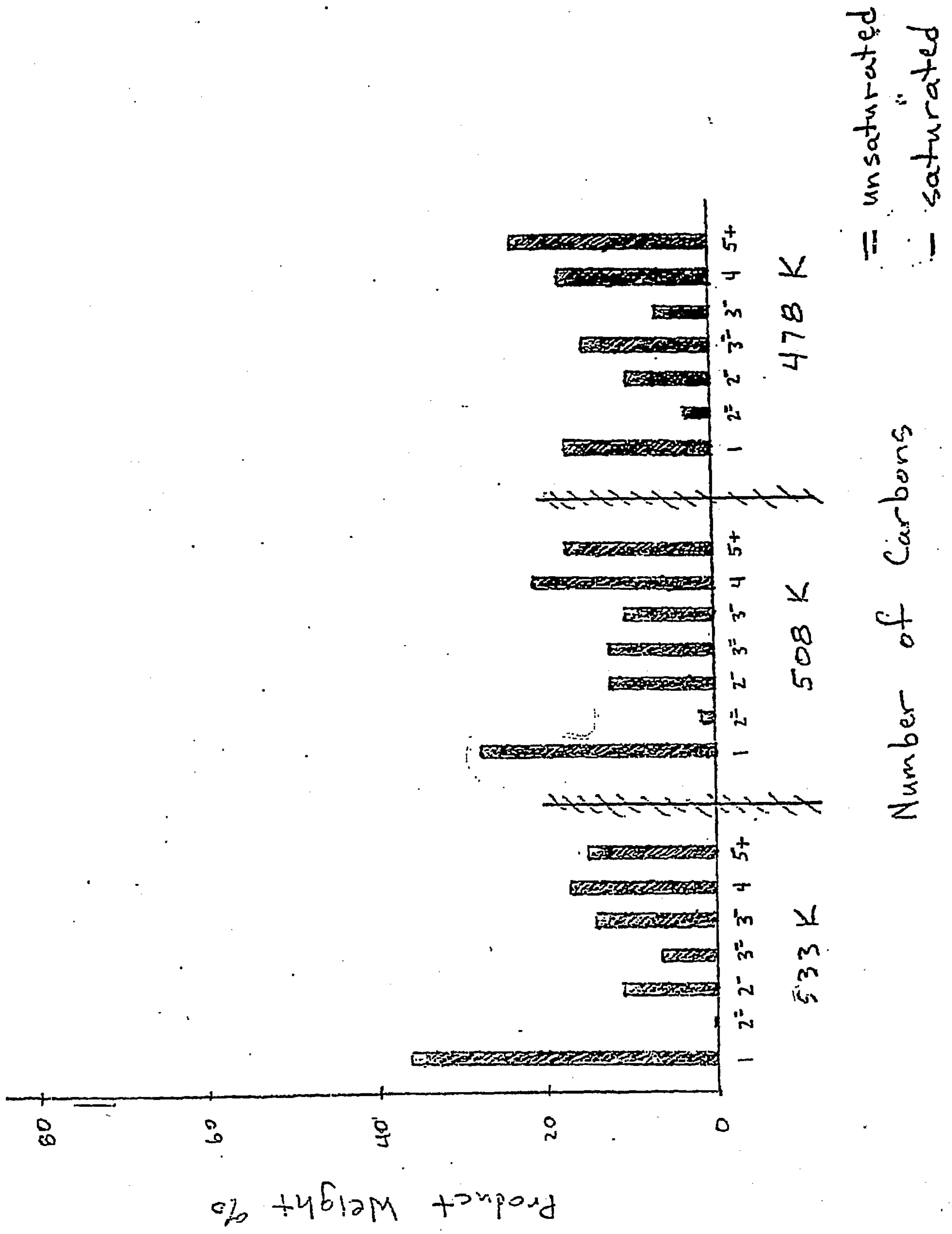

Fig 11

10%Ni/1%K/TiO$_2$ (with promoter)

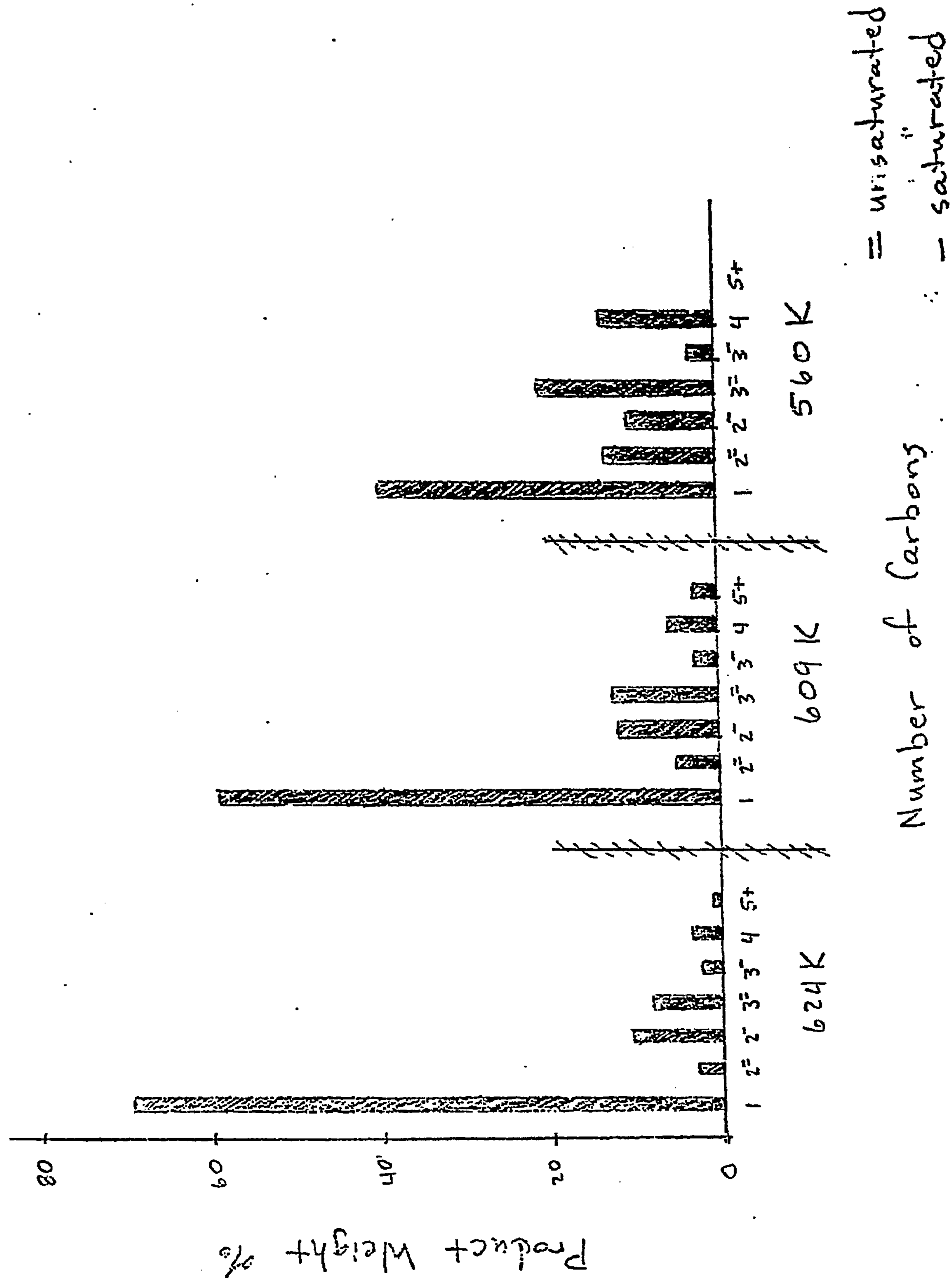

Fig 12