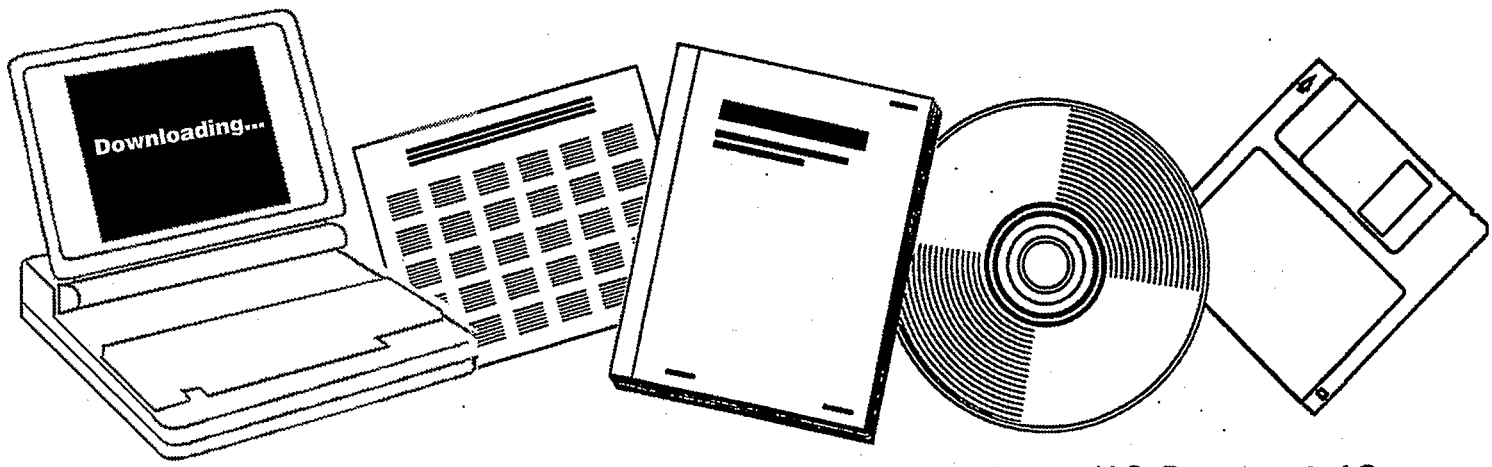
FTIR STUDIES OF HYDROCARBON SYNTHESIS ON PD/ZSM5 CATALYSTS. QUARTERLY PROGRESS REPORT

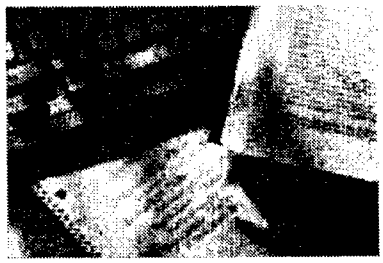
NOTRE DAME UNIV., IN. DEPT. OF CHEMICAL ENGINEERING

15 NOV 1985



One Source. One Search. One Solution.

NTIS



Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

DOE/PC/70788--T3

DE86 002829

DEPARTMENT OF ENERGY

Quarterly Progress Report

November 15, 1985

Project 84PC70788-2

FTIR Studies of Hydrocarbon Synthesis on Pd/ZSM5 Catalysts

directed by

Eduardo E. Wolf
Professor
Department of Chemical Engineering
University of Notre Dame

DISCLAIMER

BRIEF SUMMARY OF PROGRESS

During the last quarter several objectives were attained:

1) A strong dependence between the catalytic properties of Pd/ZSM5 during CO hydrogenation and the cation-exchanged form of the support has been established.

2) Steady-state kinetic and spectroscopic results were duplicated for the same system under transient conditions.

3) Infrared spectra indicates that the structure of adspecies present during CO hydrogenation may be related to production rate and selectivity.

SUMMARY OF PROGRESS

The CO hydrogenation properties of Pd on ZSM5 has been found to be dependent on the cation present on the support. As seen in figures 1-2, the rate of hydrocarbon production, which is comparable for the H and Na forms, increases significantly when La-ZSM5 is employed as the support. The accompanying variation in the line slopes (i.e. activation energies) suggests a relation between support and reaction rate. The product distribution also depends on the ion-exchanged form of the zeolite (figures 3-5). At present, only Pd/Na-ZSM5 has produced measurable quantities of oxygenates. This significant change in the product distribution indicates that the reaction pathway may depend on the nature of the support.

In the study of the Pd/Na-ZSM5, the kinetic and spectroscopic nature of the catalyst was monitored under transient conditions. Activity and IR measurements taken during a temperature-programmed reaction or TPR (a linear increase in temperature with time) agreed with those determined at steady-state (figure 2). TPR-IR results were also comparable with steady state observations. This technique provides the means for rapid data collection under a wide range of conditions.

Infrared spectra of the catalysts under reaction conditions also vary with support composition (figures 6-8). In the formyl/formate region

(1750-1500 cm^{-1}), the Pd/Na-ZSM5 (figure 6) shows strong absorbance at 1709, while both H (figure 7) and La forms (figure 8) exhibit bands between 1550 and 1600 cm^{-1}. This finding may increase the understanding of the drastic change in selectivity between the former and latter systems. A similar difference in spectra exists in the methoxy/methyl region (1500-1350 cm^{-1}). Bands on the Na form at 1446 and 1381 differ in location and number from those found on the Pd/H-ZSM5 and Pd/La-ZSM5, again pointing towards support-dependent catalyst properties. To investigate the nature of the adsorbed species, various vapor phase species were deposited on Pd/Na-ZSM5 and pure Na-ZSM5 wafers. The bands generated by formic acid (1709 cm^{-1}), dimethyl ether (1447 cm^{-1}), and methanol (1380 cm^{-1}) led to the assignment of the peaks as formyl, methoxy, and methyl groups respectively. The results also indicate that all three species are present on the Na-ZSM5 support itself, which leads directly to the conclusion that it is an important factor in the course of the reaction.

Current work concerns the peak assignment on H and La forms of the catalysts. Other transient methods (concentration and pressure ramps) will be used to study the effect of other cation-exchanged supports on Pd-catalyzed hydrogenation of CO.

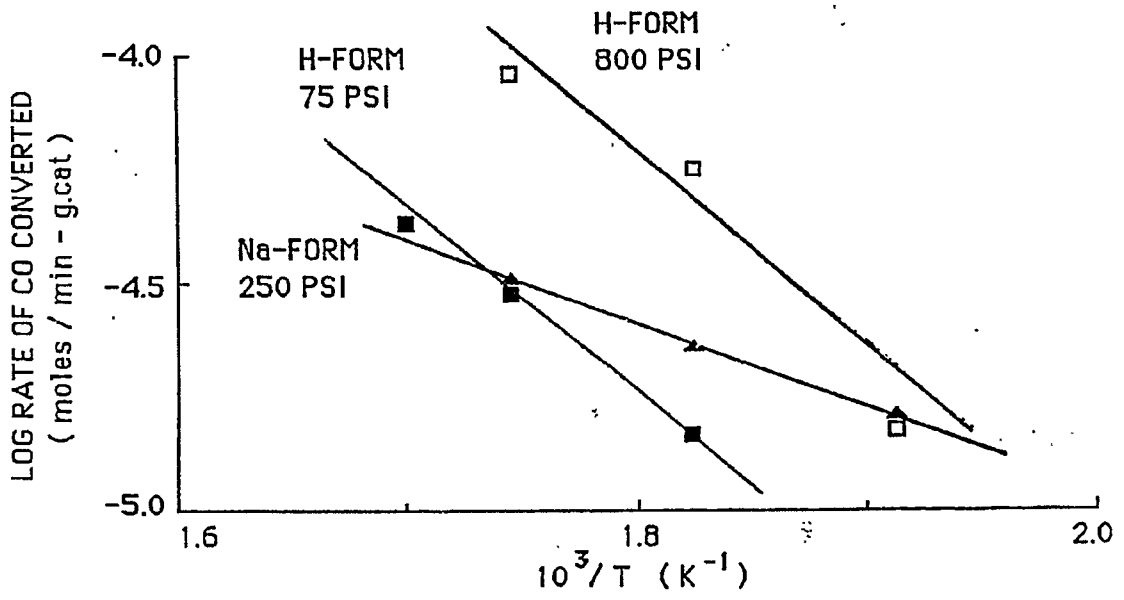


FIGURE 1 ARRHENIUS PLOT FOR 2% Pd/H-ZSM5 AND 2% Pd/Na-ZSM5 AT VARIOUS PRESSURES $H_2/CO=2$

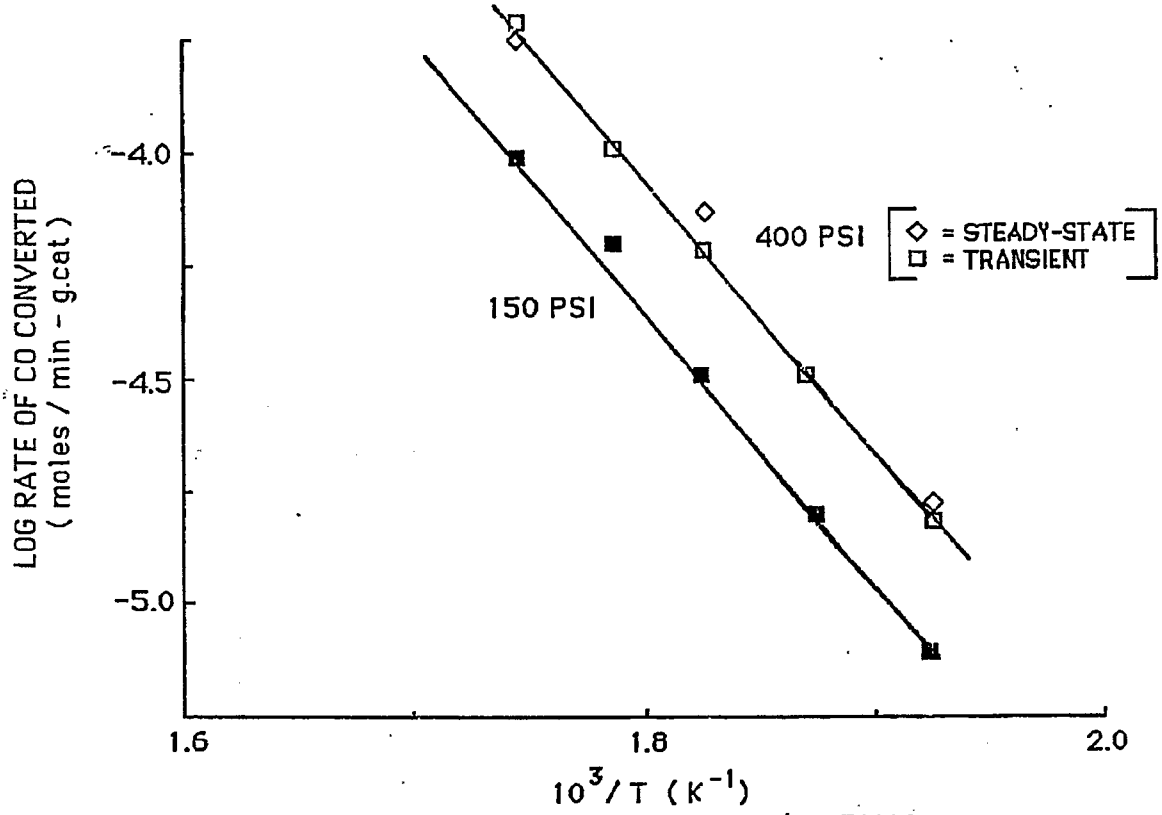


FIGURE 2 ARRHENIUS PLOT FOR 2% Pd/La-ZSM5 AT VARIOUS PRESSURES $H_2/CO=2$

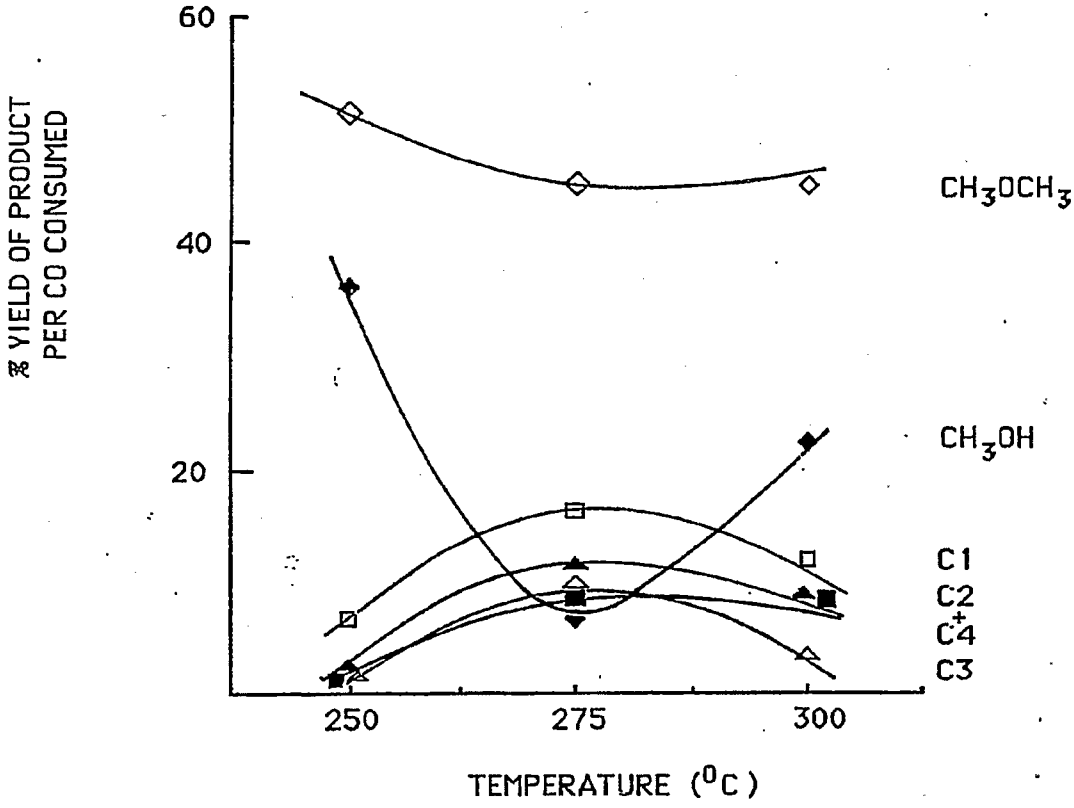


FIGURE 3 SELECTIVITY VS. TEMPERATURE FOR 2% Pd/Na-ZSM5
PRESSURE=250 PSI $H_2/CO=2$

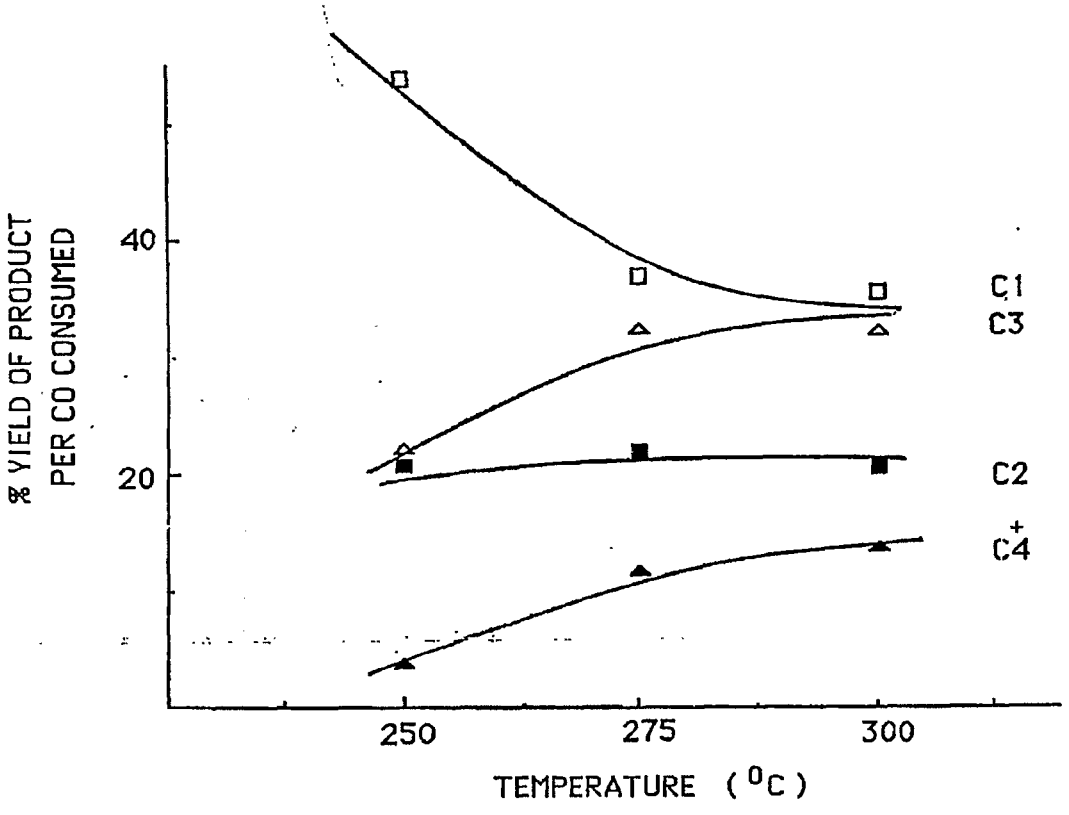


FIGURE 4 SELECTIVITY VS. TEMPERATURE FOR 2% Pd/H-ZSM5
PRESSURE=800 PSI $H_2/CO=2$

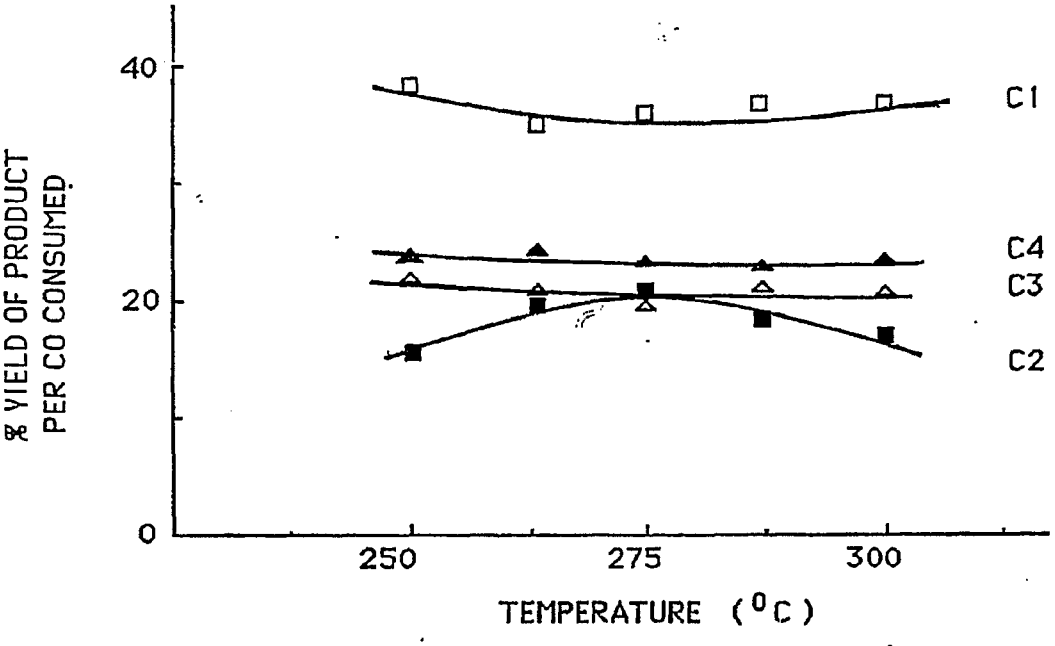


FIGURE 5 SELECTIVITY VS. TEMPERATURE FOR 2%Pd/La-ZSM5
PRESSURE=150 PSI $H_2/CO=2$

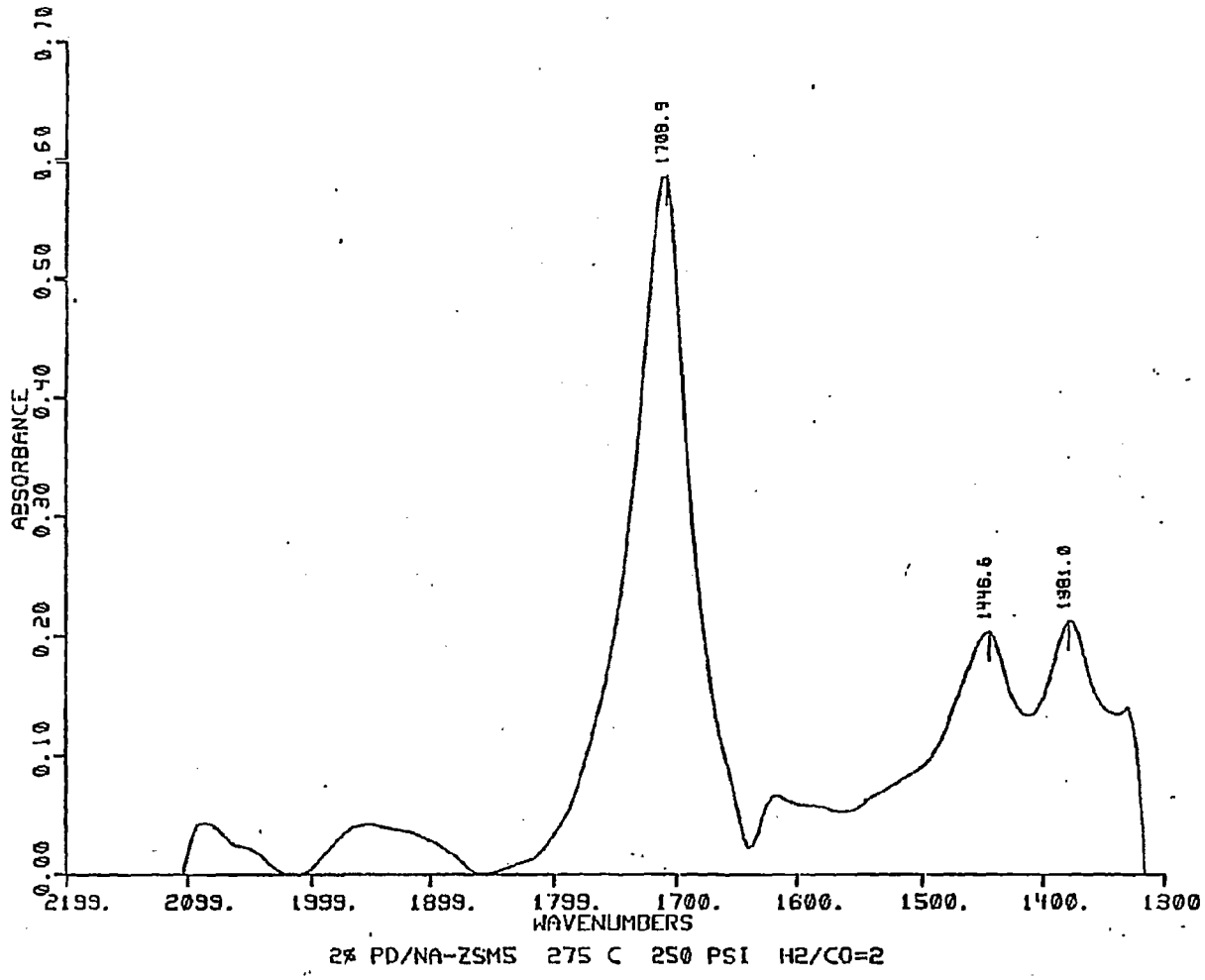

ABSORBANCE
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
1708.9
1446.9
1381.0
2199.
2099.
1999.
1899.
1799.
1700.
1600.
1500.
1400.
1300.
WAVENUMBERS
2% PD/NA-ZSM5 275 C 250 PSI H2/CO=2

FIGURE 6

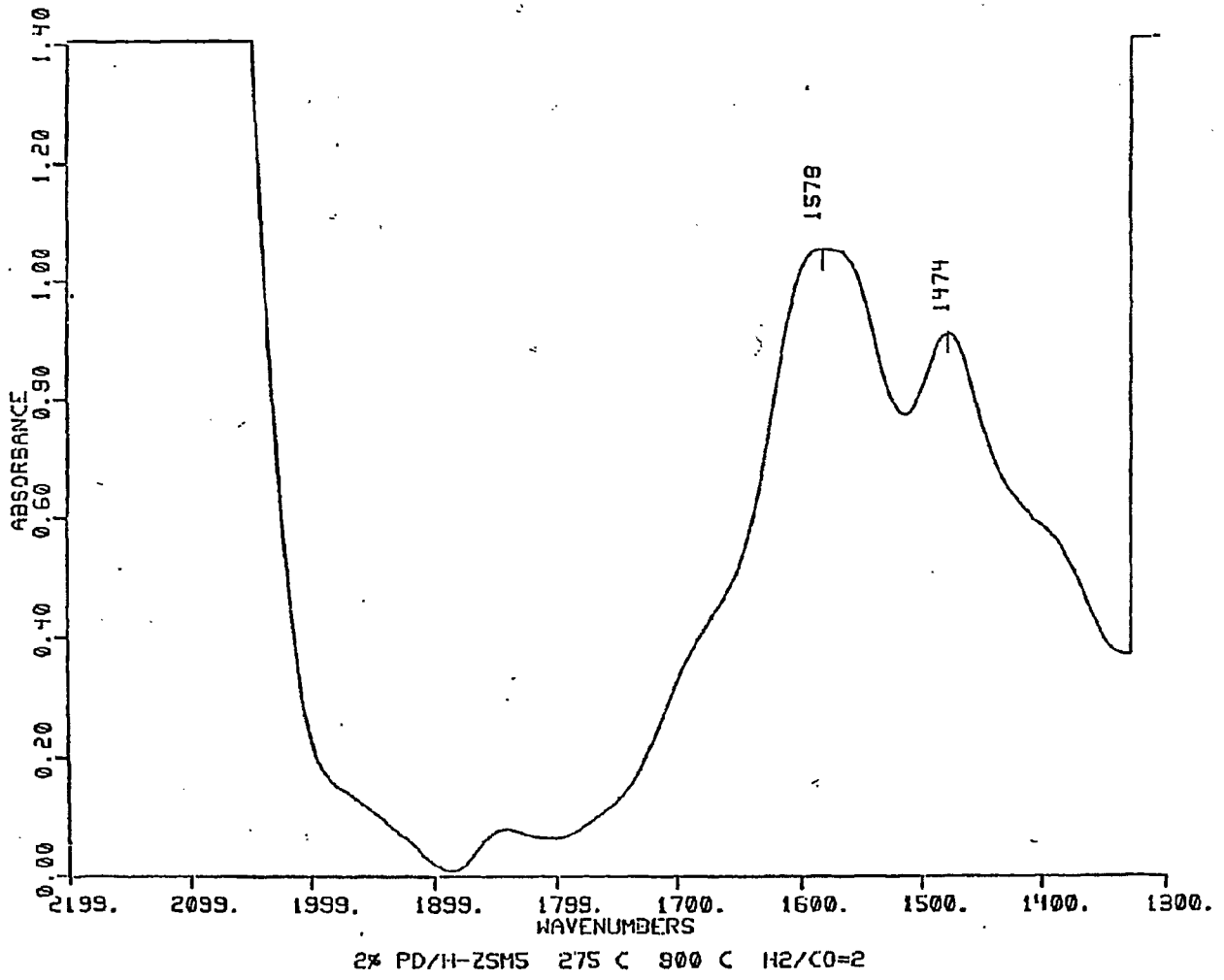

ABSORBANCE
0.00
0.20
0.40
0.60
0.90
1.00
1.20
1.40
1578
1474
2199.
2099.
1999.
1899.
1799.
1700.
1600.
1500.
1400.
1300.
WAVENUMBERS
2% PD/H-ZSM5 275 C 800 C H2/CO=2

FIGURE 7

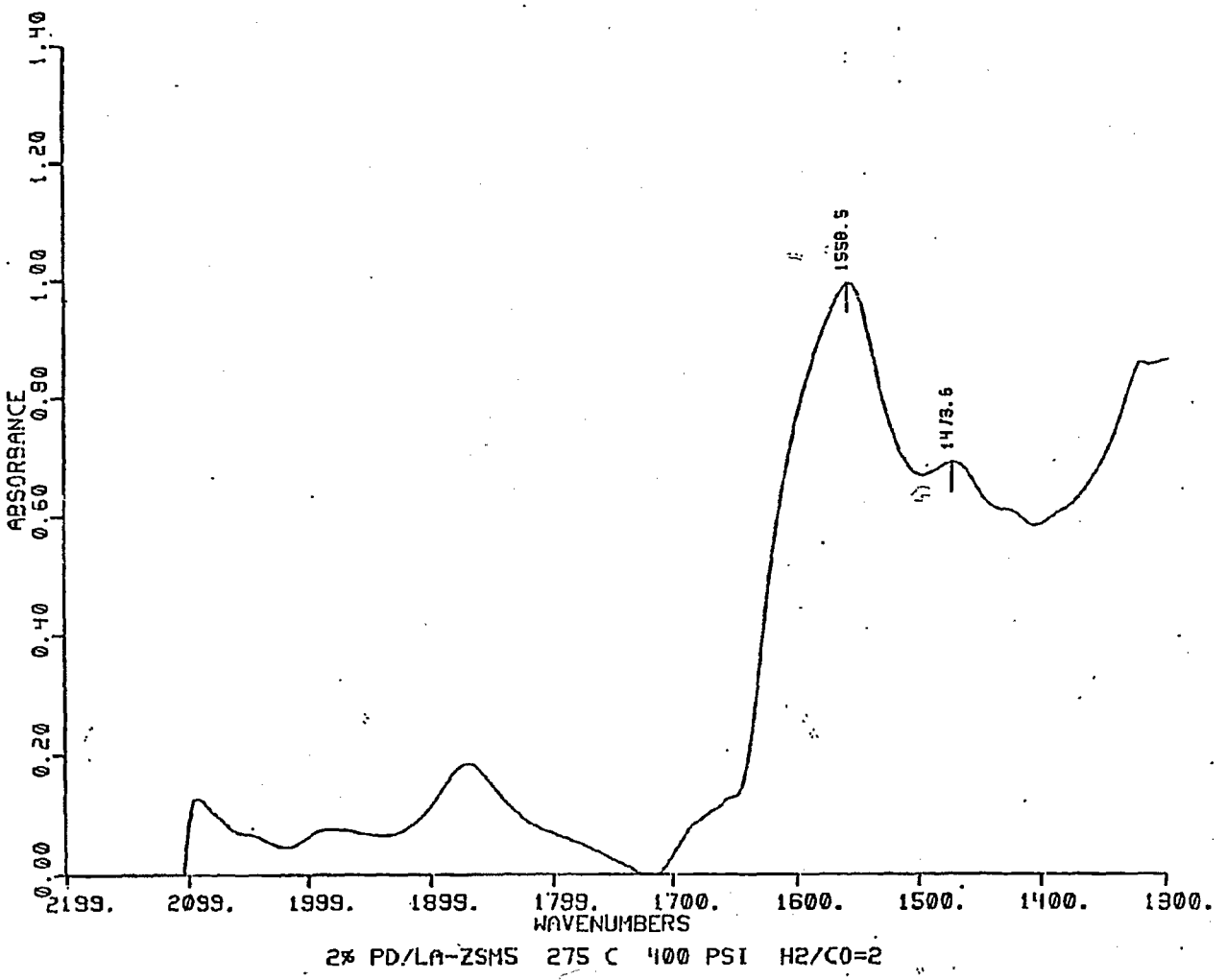

ABSORBANCE
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1558.5
1473.6
2199.
2099.
1999.
1899.
1799.
1700.
1600.
1500.
1400.
1300.
WAVENUMBERS
2% PD/LA-ZSM5 275 C 400 PSI H2/CO=2

FIGURE 8

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000