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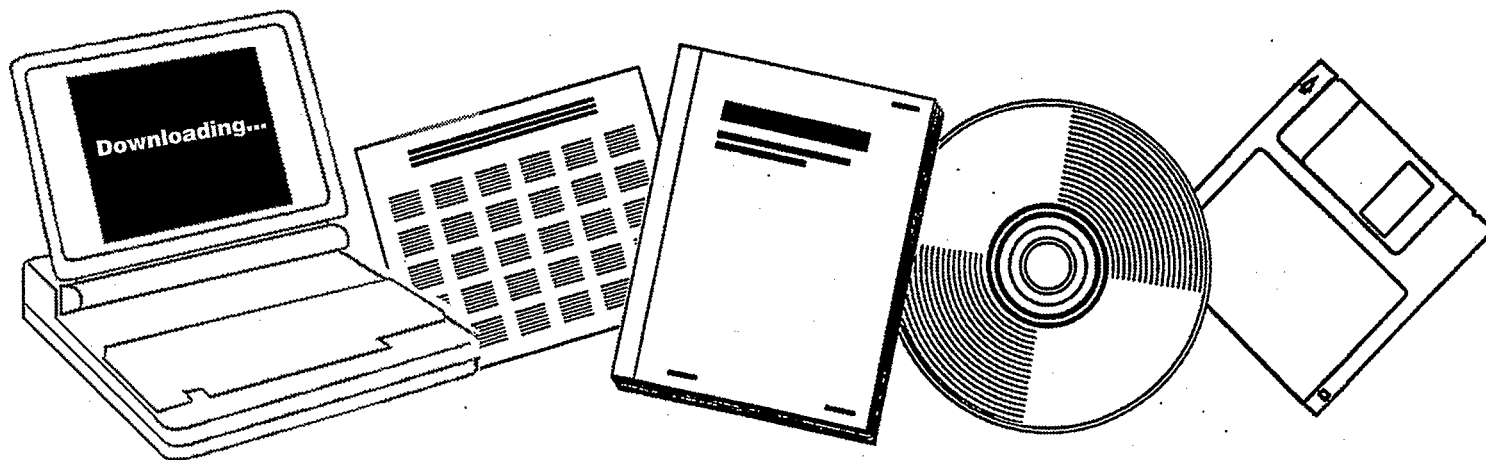
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FTIR STUDIES OF HYDROCARBON SYNTHESIS ON PD/ZSM5 CATALYSTS. QUARTERLY PROGRESS REPORT

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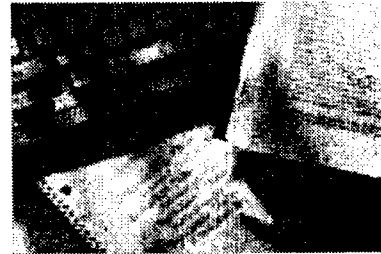
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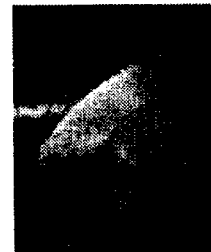
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DEPARTMENT OF ENERGY
Quarterly Progress Report

November 15, 1985

Project 84PC70788-2

FTIR Studies of Hydrocarbon Synthesis
on Pd/ZSM5 Catalysts

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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.

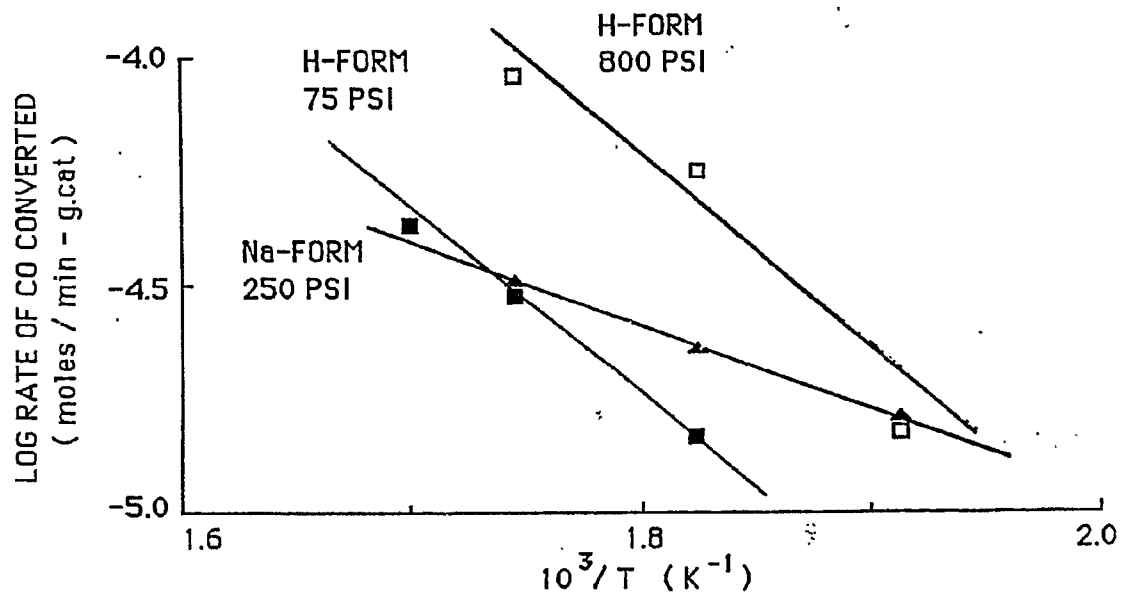


FIGURE 1 ARRHENIUS PLOT FOR 2% Pd/H-ZSM5 AND 2% Pd/Na-ZSM5 AT VARIOUS PRESSURES $H_2/CO=2$

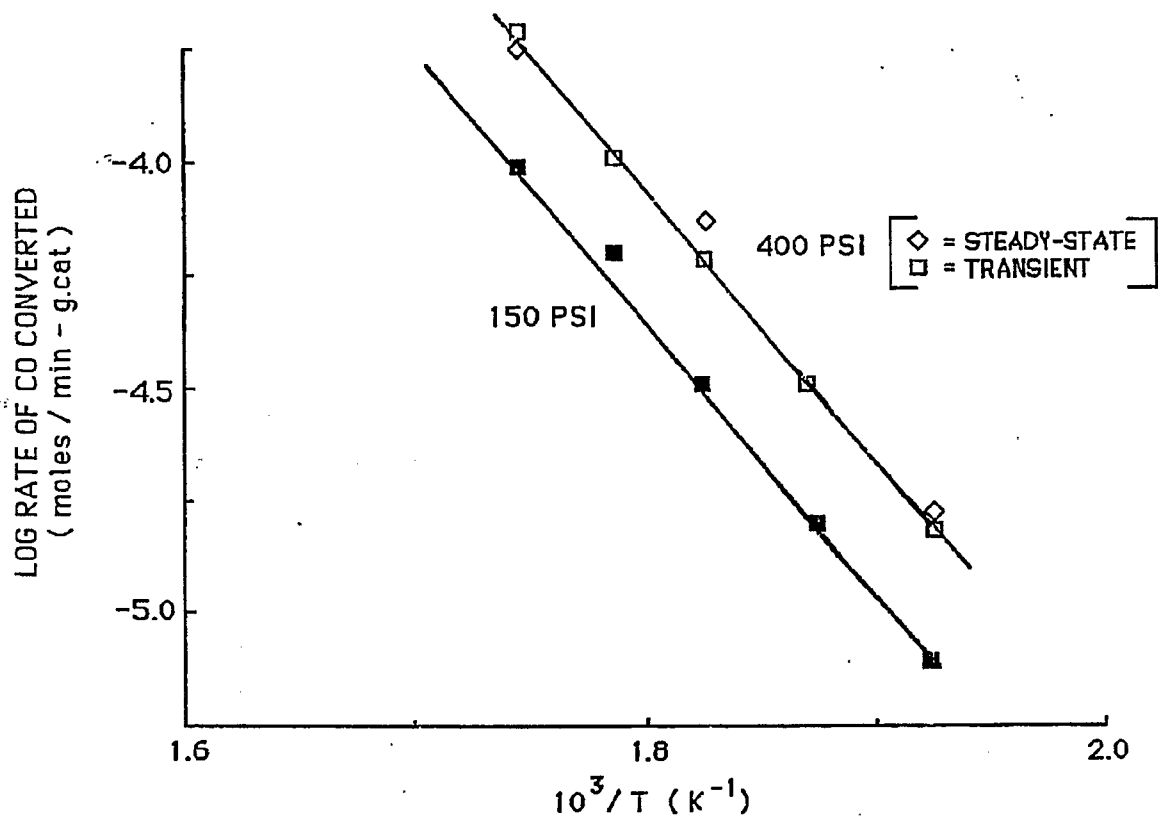


FIGURE 2 ARRHENIUS PLOT FOR 2% Pd/La-ZSM5 AT VARIOUS PRESSURES $H_2/CO=2$

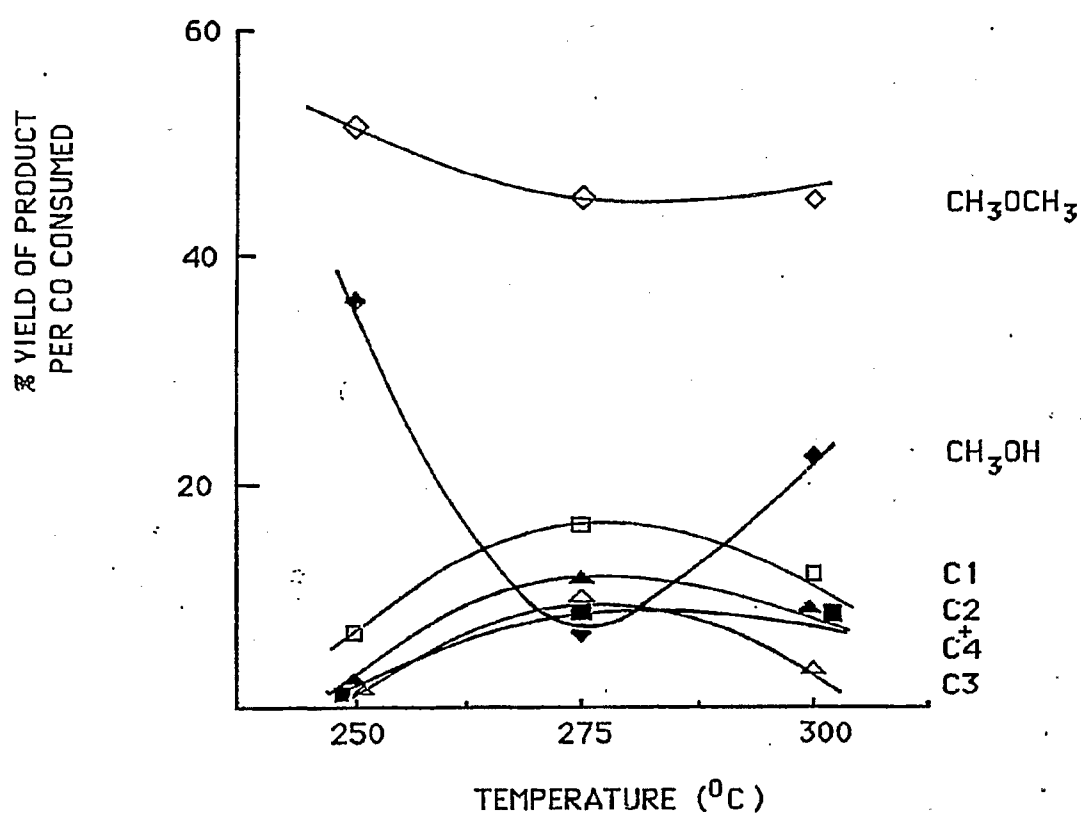


FIGURE 3 SELECTIVITY VS. TEMPERATURE FOR 2% Pd/Na-ZSM5
 PRESSURE=250 PSI H₂/CO=2

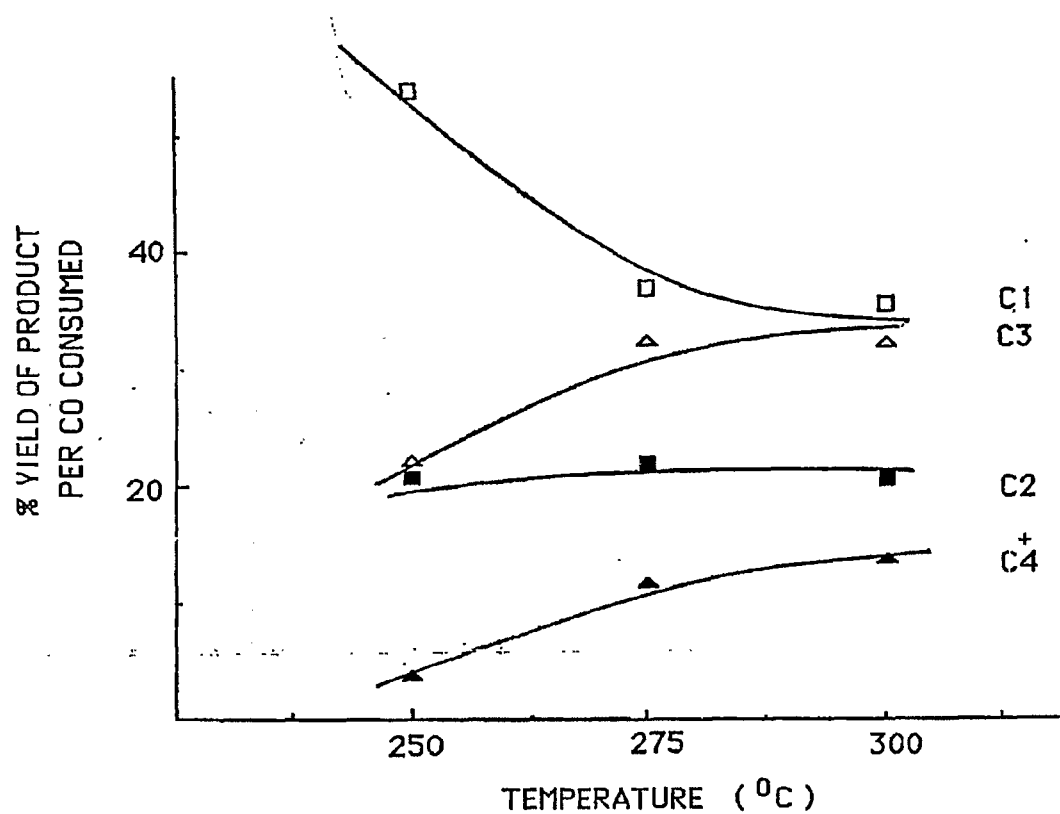


FIGURE 4 SELECTIVITY VS. TEMPERATURE FOR 2% Pd/H-ZSM5
PRESSURE=800 PSI $H_2/CO=2$

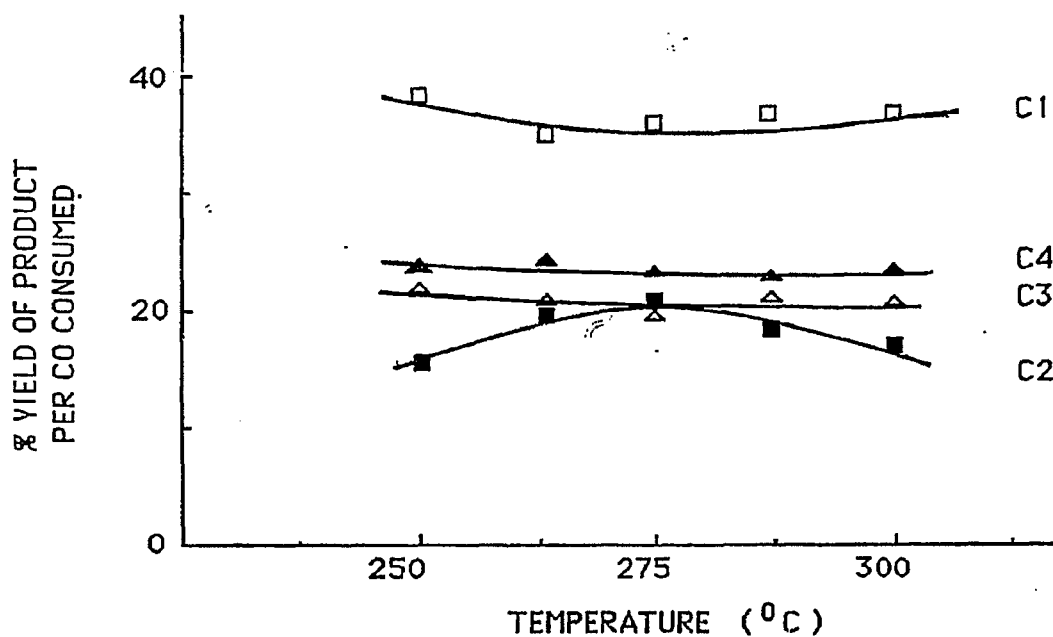


FIGURE 5 SELECTIVITY VS. TEMPERATURE FOR 2% Pd/La-ZSM5
PRESSURE=150 PSI $H_2/CO=2$

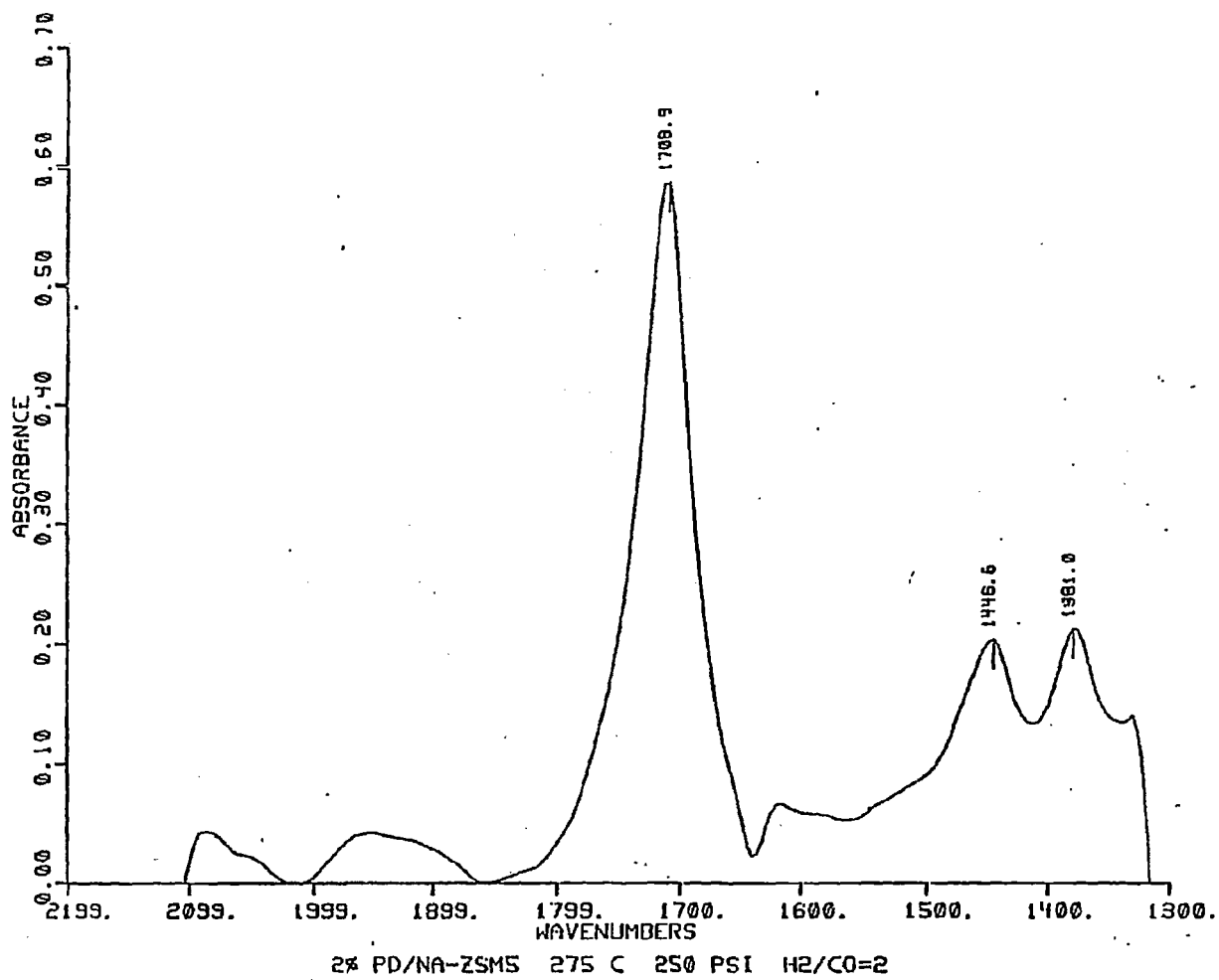


FIGURE 6

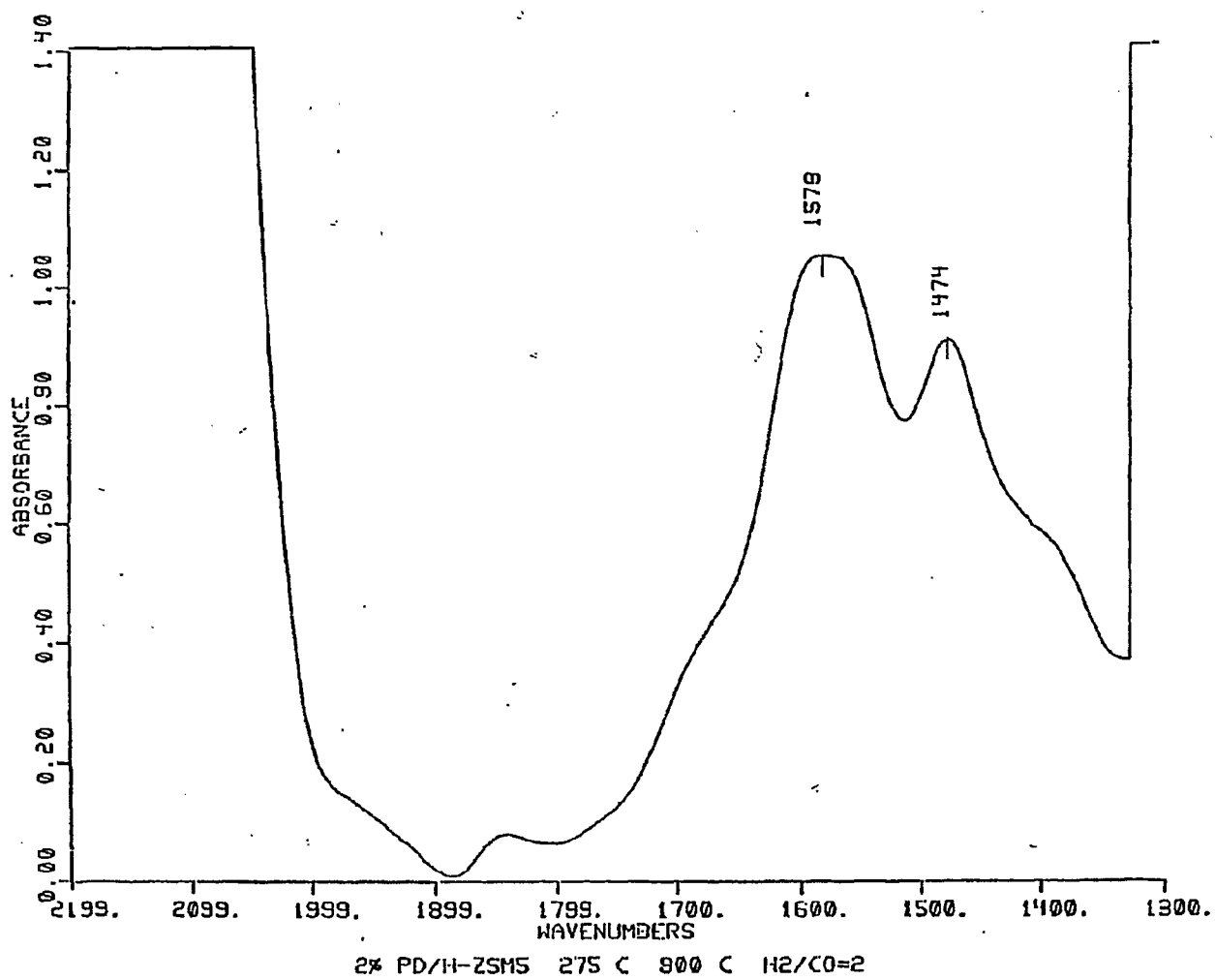


FIGURE 7

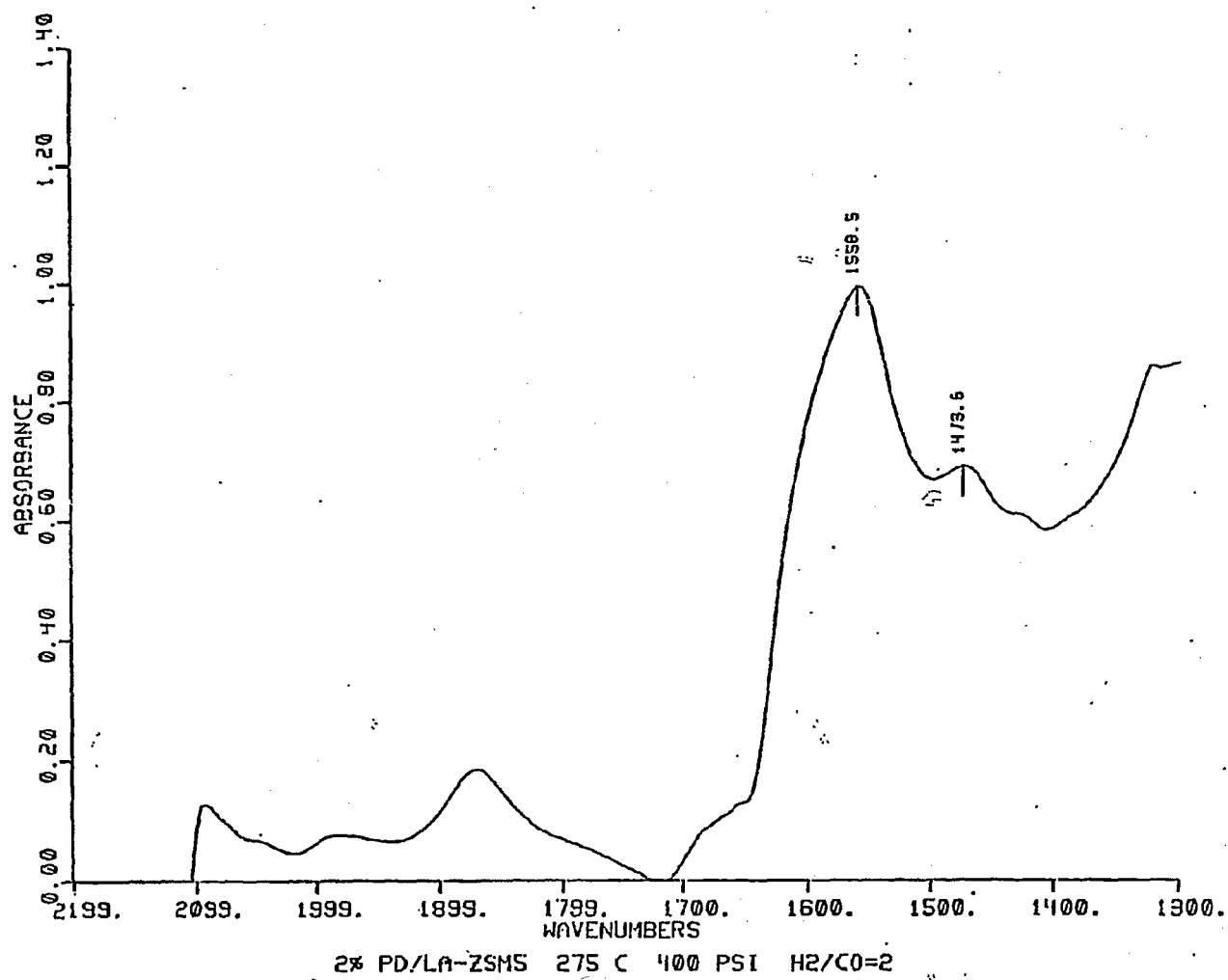


FIGURE 8

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