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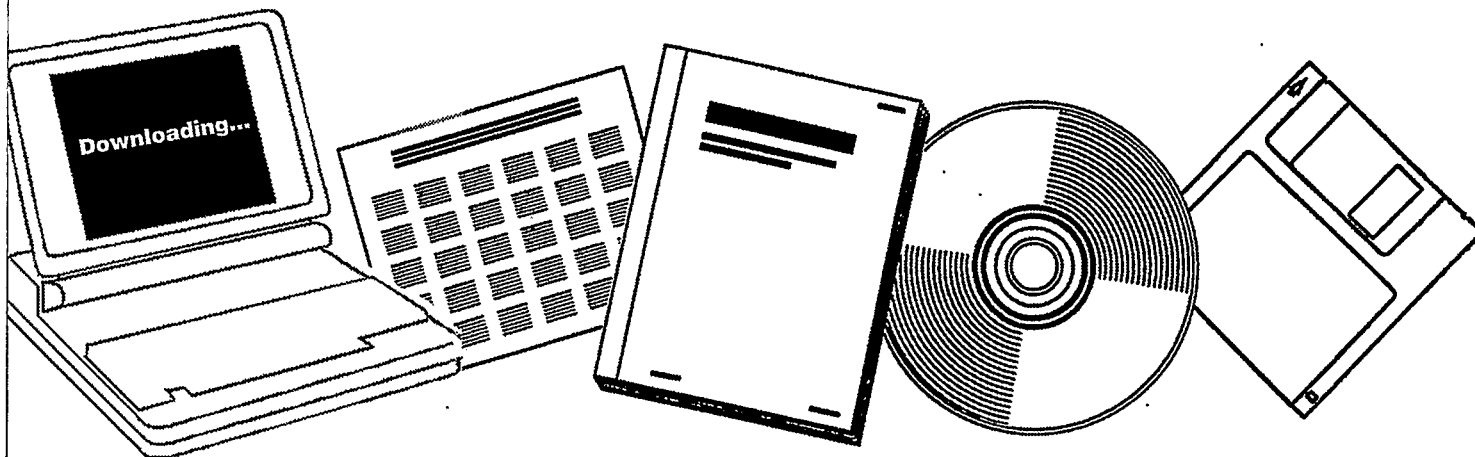
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KINETICS AND FTIR STUDIES OF HYDROCARBON SYNTHESIS ON PD/ZSM5 CATALYSTS. FINAL REPORT

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ENGINEERING

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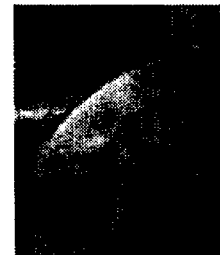
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FTIR Studies of Hydrocarbon Synthesis
on Pd/ZSM5 Catalysts

directed by

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Kinetics and FTIR Studies of
Hydrocarbon Synthesis on Pd/ZSM5 Catalysts

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Abstract

Hydrocarbon synthesis during CO hydrogenation over Pd/M-ZSM5 (M=H,Na,La) and Pd/SiO₂ has been investigated. Overall activity depended on the cation-exchanged form of the support and decreased in the order Pd/La-ZSM5 = Pd/Na-ZSM5 > Pd/H-ZSM5 > Pd/SiO₂. The zeolite-supported catalysts showed high selectivity towards saturated C₂-C₆ hydrocarbons, whereas Pd/SiO₂ favored methanol production. Increasing temperature and H₂/CO feed ratio led to higher reaction rates, lower yields of C₂-C₆ products, and increased lighter hydrocarbons. A mechanical mixture of Pd/SiO₂ and Na-ZSM5 showed similar product distribution as Pd/Na-ZSM5. Infrared spectra of the catalysts under reaction conditions indicate the presence of adsorbed oxygenates on the zeolite.

Changes in the IR bands during the initial stages of the reaction suggest that surface species on the zeolite are not methanol synthesis intermediates. The effects of various temperatures and H₂/CO ratios on the spectra are small. The kinetic and infrared results indicate that C₂+ hydrocarbons synthesis over Pd/ZSM5 follows a bifunctional reaction pathway, involving methanol synthesis over Pd and conversion of methanol to hydrocarbons on the zeolite support.

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INTRODUCTION

The conversion of synthesis gas to methanol over supported palladium has been the subject of many recent studies (1-8). An attractive property of this catalyst is its selectivity for methane and methanol production during CO hydrogenation. The nature of the support, as well as the presence of promoters, strongly affects the activity and selectivity of these catalysts (1-8). Under certain conditions, Pd impregnated on acidic carriers such as alumina and silica-alumina was found to be more active for MeOH synthesis than when the metal was deposited on silica (3). The presence of alkali metals and rare earth metal oxides can also enhance the conversion of H_2/CO over palladium (3,5,8).

Interest in methanol synthesis has been renewed due to the disclosure of the Mobil process for the conversion of methanol to high-octane gasoline over zeolites (9). Syngas could be selectively converted to hydrocarbons via a two-step process. A major drawback of this route is the equilibrium limitations on the production of CH_3OH . Another route for the conversion of CO/H_2 to hydrocarbons is the Fischer-Tropsch synthesis, which yields a broad spectrum of products (10). To avoid the problems of these two processes, bifunctional catalysts have been investigated. These catalysts consist of a metal, capable of reducing CO to hydrocarbons or methanol, impregnated on a shape-selective zeolite. Several investigators have found that the formation of large (C_{12}^+) hydrocarbon products can be suppressed during CO hydrogenation over Fe (11), Ru (12), and Co (13) when supported on ZSM5. Use of a methanol synthesis catalyst on zeolites becomes feasible because equilibrium constraints of CH_3OH formation are avoided by a "drain-off mechanism" (14), which removes methanol from the gas phase by converting it to hydrocarbons. This second reaction

essentially stops the methanol decomposition reverse reaction, allowing CO conversion to proceed past the equilibrium point. This route has been shown to be viable for hydrocarbon synthesis over ZnO/ZSM5 and Zr/ZSM5 (15), as well as a physical mixture of Pd/SiO₂ and Y- zeolites (16).

The aim of this investigation is to study the synthesis of hydrocarbons over Pd/ZSM5 during CO hydrogenation, and probe the reaction pathway. Several forms of ZSM5 and one grade of SiO₂ were used as supports. The promoter effects arising from different zeolite cations, as well as the expected support effects, were analyzed. The catalysts were studied at several temperatures and H₂/CO feed ratios to ascertain the activity and selectivity. The reaction mechanism was investigated to determine if hydrocarbon synthesis occurs via a 'true bifunctional' pathway, consisting of MeOH desorption from Pd to the gas phase before its conversion over ZSM5 acid sites (14).

In situ infrared studies were also conducted using Fourier Transform Infrared spectroscopy (FTIR) in an attempt to correlate the activity results with adsorbed species. The FTIR studies were conducted at high pressure and at conditions similar to those used in the kinetic studies.

EXPERIMENTAL

Catalyst Preparation. H-ZSM5 was synthesized by and kindly supplied to us by Amoco Oil Research Laboratories. The ZSM5 supports were prepared by contacting 5.0 g of the zeolite with 250 ml of 1.0 M aqueous solution containing the chloride salt of the cation to be deposited. Heating to 60°C was used to enhance the exchange (17). After three separate contact periods, the zeolite was thoroughly washed with deionized H₂O at 90°C and dried at 100°C.

Palladium was dispersed on the supports by a wet impregnation technique (18). An appropriate amount of Palladium acetylacetonate (Pd(acac)₂) to pro-

duce a 2% loading was added to excess CH_2Cl_2 and mixed with the zeolite support. The slurry was stirred at room temperature for 24 hrs., followed by application of a low vacuum to remove the solvent. The solids were dried at 100°C overnight.

Catalyst pretreatment consisted of a high temperature calcination and reduction. The samples were heated to 600°C under flowing O_2 for 2 hours, followed by He flush while the reactor was cooled to 500°C . The catalyst was then exposed to flowing H_2 for three hours. A list of the various catalysts used and their characteristics is presented in Table 1.

Catalyst Characterization. Following pretreatment, the samples were characterized by CO chemisorption, x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Chemisorption measurements were carried out immediately after the pretreatment. When reduction was completed, the catalyst was cooled to 400°C under He and outgassed for 1 hour, followed by rapid cooling to room temperature. Pulses of CO were then injected into the flowing He stream until saturation was evident from thermal conductivity cell readings. Chemisorption experiments were only performed on fresh catalyst samples.

X-ray Diffraction. A Diano XPG-2 X-ray Diffractometer was used with Cu $K\alpha$ -radiation ($\lambda=1.542\text{\AA}$), a 3 degree beam slit, and a 0.2 degree detector slit. The source voltage and amperage were 45 kV and 30 mA, respectively. The scan rate for the survey scans of the catalysts was set at 2 degrees/min with a detector time constant of 1 second. For the x-ray line broadening calculations, a scan rate of 0.5 degrees/min with a detector time constant of 2.5 seconds was used due to the relatively low Pd loading. The XRD samples were wafers prepared by the same procedure as used in making wafers for the infrared cell reactor, but the XRD wafers were thicker and were placed on glass slides.

X-ray Photoelectron Spectroscopy. The XPS analysis was performed at the Amoco Research Center in collaboration with Dr. Theo H. Fleisch. The analysis was performed using a Hewlett-Packard 5950B ESCA Spectrometer with monochromated Al K α -radiation (energy=1486.6 eV). This instrument is equipped with in situ pretreatment chambers for oxidizing and reducing samples. XPS sample wafers were pressed from approximately 50 mg of catalyst powder. The samples were also reduced at 200°C and 500°C for two hours in the pretreatment chamber of the XPS unit to eliminate the effects of air exposure.

Activity and FTIR Studies Results. A conventional fixed-bed apparatus reactor was used to evaluate catalyst activity. A 0.2 g charge of pretreated catalyst, supported on glass wool, was placed in a stainless steel reactor. The reactor was gold plated to eliminate catalytic effects caused by the reactor wall. After N₂ outgassing, the sample was reduced at 250°C in flowing H₂ for three hours. The reactor was then pressurized with synthesis gas (H₂/CO=2.0). All kinetic data was taken during reactions at 250 psig. The gases were monitored by Brooks mass flow controllers. Product analysis was performed by on-line gas chromatography, consisting of a Varian 1400 GC, equipped with a 20 ft. Porapak Q column and FID, and a Varian 920 GC, employing a CTR I column and a TC cell detector. All effluent lines leading to the gas chromatographs were heated to 100°C. The reactions were controlled such that CO conversions did not exceed 1%.

The infrared spectra of the catalyst under reaction conditions were recorded using a stainless-steel reactor similar to that described by Kaul and Wolf (29). Catalyst wafers weighing approximately 30 mg were positioned between the CaF₂ windows. All spectra were recorded using a Digilab FTS-15C FTIR

spectrometer, by co-adding 25 interferograms taken at a resolution of 8 cm^{-1} . After obtaining a reference spectrum of the reduced catalyst at the reaction temperature and atmospheric pressure, the CO/H_2 mixture was introduced into the cell and the pressure increased to 250 psig. Spectra were recorded upon reaching steady-state.

RESULTS

Catalysts Characterization. The preparation methods employed yielded a fully reduced, low dispersion catalyst. CO chemisorption shows that the impregnated metal formed has large crystallites, especially for the La-ZSM5 and silica supports (Table 1). X-ray diffraction patterns of the catalyst samples exhibited a peak at $2\theta=40.1^\circ$, which is attributed to Pd (111). Use of the Scherrer equation with the broadening of this peak yielded higher estimates for the average particle size for the Pd/H-ZSM5 and Pd/Na-ZSM5 catalysts. The line broadening of the catalysts with large crystallites was too small to yield reliable values. Since Pd (100) faces are not observable by XRD, IR spectra of adsorbed CO at atmospheric pressure was employed to determine the Pd surface morphology. From Fig. 1, the strong absorbance at 1980 cm^{-1} , combined with only a weak shoulder at 1930 cm^{-1} , show that the metal consists primarily of Pd (100) sites.

XPS results are shown in Table 2 and 3 in terms of electron binding energies and atomic ratios respectively. In all catalysts, the binding energy of the Pd 3d $5/2$ line was close to the value of 335.1 eV corresponding to Pd^0 . The Pd/Si ratios obtained from XPS were not consistent with the crystallite size measurements obtained from CO chemisorption and XRD.

Activity. Initially, each catalyst was maintained at 250°C and 250 psig, and at a H_2/CO ratio of 2.0. Steady-state was reached after an induction period,

the length of which depended on the nature of the support. Figure 2 shows that Pd/La-ZSM5 required 30 hrs on-stream before product yields reached constant levels. The other catalysts attained steady-state after 8 hours, and showed similar transient behavior. Overall activity during this period increased slightly. Throughout the induction period, methane yield remained essentially constant, while C₂-C₆ hydrocarbons increased and oxygenate production showed a corresponding decrease. After reaching steady-state, the activity and product distributions were found to be nearly constant for at least 72 hours.

At the initial temperature and pressure, a strong influence of the support on activity and yields was established. As seen in Figure 3, the overall activity decreased in the order Pd/La-ZSM5 = Pd/Na-ZSM5 > Pd/H-ZSM5 > Pd/SiO₂. The turnover numbers reflect a strong dependence on the zeolite cation, decreasing in the order Pd/La-ZSM5 > Pd/Na-ZSM5 > Pd/SiO₂ = Pd/H-ZSM5. Fig. 4 shows that the zeolite-supported catalysts produced hydrocarbons up to C₆ and oxygenates, while Pd/SiO₂ yielded only CH₄ and CH₃OH, with only traces of C₂. Figure 4 shows that Pd/La-ZSM5 and Pd/Na-ZSM5, which showed approximately equal activity, converted CO to C₂₊ hydrocarbons at yields exceeding 80%. Among the higher molecular weight products, almost equal selectivity towards C₅ and C₆ was seen, with only negligible amounts of C₇₊ aliphatics, and no aromatics. The Pd/H-ZSM5, which showed greater yields for lighter hydrocarbon products, had significantly lower activity than the other zeolite-supported catalysts. In all cases for Pd/ZSM5, only a small fraction of olefins were found in the hydrocarbon products. Also, dimethyl ether (DME) accounted for the oxygenated species formed during the reaction on ZSM5 supports. Under all conditions, the product streams showed no detectable CO₂ production.

Therefore, it is important to note that all yields are expressed as % CO converted, rather than % hydrocarbons alone.

The effect of temperature on the product distributions is seen in Fig. 5. Generally, a decrease in both higher hydrocarbon (C_2+) and oxygenate yields accompanies the increase in the lighter end CH_4 . Since DME levels are low, the Pd/Na-ZSM5 catalyst exhibits an almost equal decrease in C_2-C_6 yield with increasing CH_4 production. Methane shows higher yield at the expense of DME over Pd/H-ZSM5, with higher hydrocarbons remaining relatively constant. Changes in yield follow different trends over the La-ZSM5 supported catalyst. The light products show a linear increase in yield, but C_2+ product yield drops off sharply at 300°C. This characteristic may be directly linked to the unexpected increase in DME yield at 300°C. The Pd/SiO₂ catalyst exhibits the most pronounced trade-off between light hydrocarbons and oxygenates, indicating that the observed temperature effects reflect changes in the reaction(s) taking place on the metal.

Reaction rates also increased with decreasing concentration of gas-phase CO. As seen in Figure 6 a four-fold increase in the H_2/CO ratio led to a doubling of the rate of CO converted over Pd/La-ZSM5 and Pd/Na-ZSM5. Considerably less sensitivity was seen in the Pd/H-ZSM5 case. Product distributions were found to be very dependent on the H_2/CO ratio. Figure 7 shows that an increase in the hydrogen concentration results in higher yields of DME in the product stream, at the expense of higher hydrocarbons. Methane production varies only slightly under these conditions, suggesting that the production of lighter hydrocarbons is independent from the synthesis of higher molecular weight products.

As a means of investigating the effect of strong acid sites in the Pd/ZSM5

catalysts, Pd/SiO₂ and pure Na-ZSM5 zeolite were mechanically mixed such that metal/zeolite ratio was the same as that in the Pd-impregnated Na-ZSM5 catalyst. The overall activity of this admixture exceeded that of the Pd/SiO₂, but was significantly less than any zeolite-supported catalyst. The yields, shown in Figure 8, have the same relative distribution of hydrocarbons in the C₂-C₆ range for the physically mixed system as for the impregnated Pd/Na-ZSM5 catalyst. Since Pd/SiO₂ produced only CH₄ and CH₃OH, the acid sites of the ZSM5 are responsible for the conversion of methanol to hydrocarbons. However, the admixture produced much greater proportions of methane and oxygenates.

Increasing flow rates does not affect overall CO conversion and DME production remain constant at low flow rates (Fig. 9). However the yield of DME increases significantly at low residence times (high flow rates). At this point, the hydrocarbon fraction contains about 50% olefins, indicating that these species are produced during reaction but they are not hydrogenated under these conditions.

Infrared Results. Infrared spectra of the adsorbed species of the catalysts, as seen in Figure (10), were collected at a temperature of 250°C, pressure equal to 250 psig, and H₂/CO feed ratio of 2. To establish the nature of CO bonded to the Pd crystallites during the reaction, the gas-phase CO peak was subtracted from the spectra. The results shown in Fig. 10, shows that the 1960 cm⁻¹ band due to bridge-bonded CO, is more intense than that from CO bonded linearly, found at 2080 cm⁻¹.

Minor bands located at 1850-1900 cm⁻¹ region are also observed in the Pd/La-ZSM5 and Pd/H-ZSM5 which also exhibit bands at 1580 and 1480 cm⁻¹. The spectrum obtained on the Pd/Na-ZSM5 catalyst exhibit bands at 1710, 1640, 1590 cm⁻¹, a doublet at 1475-1458 cm⁻¹, and a smaller band at 1380 cm⁻¹.

Infrared spectra was collected during the induction period every 10 minutes on the Pd/Na-ZSM5 catalyst, in order to establish changes in surface species. Fig. 11 shows that the bridge bonded CO band remains fairly constant (gas phase CO was not subtracted in these spectra). The bands at 1640 cm^{-1} decreased slightly whereas bands at 1480, 1380 and 1710 cm^{-1} increased especially the latter one.

The effect of temperature on the Pd/Na-ZSM5 spectra was examined using a temperature-programmed reaction. IR spectra obtained during this experiment in the temperature range 250°C-300°C, shown in Fig. 12, showed no significant changes in the position or intensity of the peaks. The effect of CO partial pressure on the IR bands was also studied at 250°C, 250 psig and at various H_2/CO ratios. As Fig. 13 shows (gas phase CO not subtracted), there is a little change in the CO bridge bonded band, and some changes in the low frequency bands. The latter are the result of changes occurring during the induction period as shown in Fig. 11 rather than due to changes in the CO/H_2 ratio.

Depositions of formic acid and dimethyl ether were performed on Na-ZSM5 to confirm the peak assignments for the Pd/Na-ZSM5 spectra. Figure 14 shows that the peak positions correlate very well with those of the catalyst under reaction conditions. This result supports not only the structural assignments, but shows conclusively that the species are present on the zeolite.

DISCUSSION

The large difference between the hydrocarbon distributions reported in this study and those of previous work (1-8) for palladium catalysts suggests that the reactions pathway is altered by the ZSM5 zeolite. Pd supported on acidic carriers such as Al_2O_3 has been reported to selectively synthesize DME

during CO hydrogenation, while producing small amounts of C_2+ (2). Bronstead acid sites on ZSM5 supports convert oxygenates, such as DME, to hydrocarbon products, the distribution dependent on temperature and reactant partial pressure (15,19). Therefore, the observed products are formed from a multistep pathway, employing both metal and zeolite catalytic sites.

The role of the Pd crystallites and ZSM5 supports must be established to account for variations in the catalyst performance. The reported rates for CO hydrogenation over supported Pd (1-8) and MeOH conversion over ZSM5 (15,19) indicate that the latter reaction is much more rapid. This "drain-off" of the initial reaction products suppresses any reverse reaction (MeOH decomposition). Therefore, methane production and methanol synthesis on Pd must be the rate-determining step for CO consumption. Given the selectivity of CO hydrogenation over Pd, the formation of C_2+ hydrocarbons must take place exclusively on the ZSM5. Once the hydrocarbons have been formed, the hydrogenation/hydrogenolysis capabilities of the metal may influence the final products. Therefore, changes in the Pd crystallites are reflected in the overall activity, and the active zeolite sites strongly, but not solely, affect the C_2+ product distribution.

The catalysts used in this study exhibit characteristic activity trends for supported palladium. The Pd/SiO₂ selectively produced methanol and DME, which was converted to hydrocarbons on the Pd supported on the ZSM5 catalysts. This finding is in agreement with the previous conclusion (21) that large Pd crystallites contain the sites for MeOH formation. The difference between chemisorption and XRD average particle size estimates arises from the inability of the latter technique to detect crystallites smaller than 40 Å. Therefore, the estimate from XRD yields a higher value.

Among the four catalysts studied, the cation exchanged onto the ZSM5 can affect the dispersion of the metal as well as its intrinsic specific activity. The overall rate of CO consumption decreases according to $\text{Pd/La-ZSM5} > \text{Pd/Na-ZSM5} > \text{Pd/H-ZSM5} > \text{Pd/SiO}_2$; however, according to Table 1, the dispersion of the Pd/SiO_2 and Pd/La-ZSM5 catalysts are significantly lower than for Pd supported on H-ZSM5 and Na-ZSM5, which have comparable dispersion. Consequently, when rates are compared on the basis of turnover numbers for CO consumption (Fig. 3), the specific activity of the Pd/La-ZSM5 catalysts becomes about an order of magnitude higher than those of the other catalysts. The TON of the Pd/Na-ZSM5 catalysts is also higher than Pd/H-ZSM5 which indicates that the cation is promoting CO consumption on the metal, which has been previously reported for the Na- and La- doped Pd/SiO_2 catalysts (3,5). The XPS results indicate that the surface atomic % Na is similar to the Al atomic % whereas the at. % La is significantly much higher. These results suggest that while Na was ion-exchanged onto the ZSM5 zeolite, La was certainly not. Further work is underway to determine the location of the cations in relation to the metal in an attempt to determine the nature of the promotional effect. The formation of special sites due to decoration of the support by La suboxides, as it has been reported by others (33), is a possible mechanism for La promotion, whereas this does not seem to be the case for Pd/Na-ZSM5 .

The observed increase in CH_4 yields with temperature results from the competing CH_4 and CH_3OH synthesis reactions. Methanation has been found to be both kinetically and thermodynamically more favorable at higher temperatures (18). At constant total pressure, the overall CO conversion rate increased with H_2/CO ratio, (Fig. 6), which is predicted by several rate equations for supported Pd (4,6). For the hydrogenation of CO to either CH_4 or CH_3OH , the

rate is proportional to $[H_2]^a$, $[CO]^b$, with $a > b$. An increase in the H_2/CO ratio thus results in higher Pd activity.

The C_2+ hydrocarbon distributions over the Pd/ZSM5 catalysts result from the conversion of methanol on the zeolites. Although a high degree of aromatics may be formed over ZSM5 during MeOH conversion, Chang (15) has shown that low temperature and reactant partial pressure shift selectivity in favor of the C_2-C_5 fraction. Therefore, the absence of C_7+ and aromatic products is not surprising. The light hydrocarbons produced on ZSM5 which should consist mainly of olefins, are hydrogenated to alkanes on the Pd metal sites, resulting only in a small concentration of unsaturates in the effluent stream. Weak acid sites on ZSM5, which can dehydrate MeOH, account for the selectivity of DME in the oxygenated products. Variations in the hydrocarbon distributions among the Pd/ZSM5 catalysts reflect the presence of different zeolite cations (22).

The autocatalytic nature of DME conversion over ZSM5, combined with the tendency of olefins to be hydrogenated over Pd, account for some of the trends in the hydrocarbon yields. Chen and Reagan (26) have reported that the reaction of DME over the zeolite proceeds via a) dehydration of DME to light olefins, b) reaction between oxygenates and olefins to form higher olefins, and c) conversion of olefins to paraffins and higher aromatics. The autocatalytic step (b) proceeds at a much faster rate than the initiation step (a). Therefore, reduction in the olefin concentration lowers the rate of DME conversion. This suppression of the DME conversion reaction occurs through the hydrogenation of the olefins over Pd rather than step (c), which requires higher temperatures on the ZSM5 support. Increases in the DME yield with the H_2/CO ratio can also be rationalized on the basis of an increase rate of olefin

removal via hydrogenation on the metal function. The induction period observed over Pd/ZSM5 may therefore reflect either the time necessary to activate the sites for DME conversion or the time required to sufficiently deactivate the sites of olefin hydrogenation. It is interesting to note that the period of transient behavior over Pd/La-ZSM5 is similar to that found by Vannice (7) over Pd/La₂O₃ during methanol synthesis. This suggests that changes in the metal sites can be responsible for the induction period over Pd/ZSM5.

The effect temperature in the yields on the various catalysts (Fig. 4) reflects the different activation energies for the reactions involved in step a) to c). The increase in methane yield with temperature is much pronounced on the Pd/SiO₂ than on the ZSM5 supported catalysts, reflecting a lower activation energy for the methanol synthesis reaction.

The results with the Pd/SiO₂ and Na-ZSM5 admixture (Fig. 7) also confirm that gas-phase methanol is the intermediate during hydrocarbon synthesis over Pd/ZSM5. Although Pd/SiO₂ yielded only CH₄ and CH₃OH, the mixture of Pd/SiO₂ and Na-ZSM5 produced a similar C₂+ hydrocarbon distribution as the impregnated catalyst. The formation of hydrocarbons despite the separation of the two catalytic sites, shows that a gas-phase precursor is transported between the two functions. The increase in DME yield in the admixture is due to interparticle mass-transfer limitations (16), which are reduced when the metal is impregnated on the zeolite particles. The increased CH₄ in the admixture yield results from hydrogenolysis of alkanes on Pd/SiO₂ (28).

The decrease in C₂+ products with residence time (Fig. 9), while maintaining a constant rate of CO consumption, suggests that gas-phase intermediates have been removed before completion of the reaction. Higher yields

of DME and olefins imply that they are indeed intermediates. This conclusion is also supported by the autocatalytic conversion of DME over ZSM5.

While the formation of hydrocarbons involving the two separate functions is consistent with the activity and selectivity results, positive identification of the surface intermediates involved is less clear. Surface intermediates for methanol synthesis on Pd have been extensively studied and the species that have been proposed include: adsorbed CO (8), formate groups on the support (3), and formyl groups (32). Peri (8) found that absorbances in the chemisorbed CO region did not correlate to the methanol production rate on Pd/SiO₂ catalysts, which agrees partially with the results of this study. The CO absorbance on the Pd/SiO₂ catalyst was the highest, which suggests CO inhibition since this catalyst exhibited the lowest rate, and the more active zeolite-supported Pd exhibited the lowest CO absorbance and higher rates. However comparison among the zeolite-supported catalysts does not support an inverse relation with CO coverage since the CO bands remain about the same in spite of their different activities. Furthermore, significant changes in temperature and pressure are not reflected in corresponding changes in the CO bands. Thus, it appears that at the conditions used in this study, the CO bands observed do not correlate well with overall activity. The IR bands located below 1900 cm⁻¹, correspond to species located on the support, as shown by the deposition experiments. In spite of their different activities, the Pd/H-ZSM5 and Pd/La-ZSM5 catalysts exhibit the similar bands at 1585 cm⁻¹, which suggest the formation of formate groups similar to those reported by Greenler on Al₂O₃ (30). Conversely, the Pd/Na-ZSM5 and Pd/La-ZSM5 catalysts, which exhibit similar overall activity (Fig. 3), also exhibit significantly different spectrum in this region. The spectrum on the Pd/Na-ZSM5 with a strong band at

1710 cm^{-1} , resembles the spectra of formic acid adsorbed on NaY zeolites (31) rather than formate groups on ZSM5. Given the little sensitivity of the spectra to changes in operating variables (fig. 12 and 13), it is notable how these bands change during the first 40 minutes of the induction period (Fig. 12). It appears that once a certain level of the bands is attained, they remain unchanged, thus they do not seem related to reactive intermediates.

One spectral feature common to all zeolite supported catalyst, was the band located around 1475-1480 cm^{-1} . Deposition experiments with DME show the same band, and literature reports (32) assign it to C-H bending of methoxy groups. This common IR feature further supports the kinetic results which shows that hydrocarbon synthesis takes place on the support.

CONCLUSIONS

Pd/ZSM5 catalysts can selectively synthesize $\text{C}_2\text{-C}_6$ hydrocarbons from CO/H_2 . The activity and yields are very dependent on the zeolite cation, mainly due to a promoter effect on palladium. Both metal and zeolite function exhibit expected behavior with changes in the temperature and H_2/CO ratio. The performance of the physical mixture of Pd/ SiO_2 and zeolite, as well as that of Pd/Na-ZSM5 at high flow rates, indicates that methanol desorbs from the metal before its conversion to hydrocarbons. Therefore, the reaction of CO/H_2 to the observed products follows a bifunctional reaction pathway.

Figure 15 summarizes the roles of metal and zeolite sites. Following methanol synthesis, dehydration to DME takes place on weak acid sites of the zeolite. Conversion of this oxygenate on strong acid centers results in the formation of $\text{C}_2\text{-C}_6$ olefins, which are hydrogenated to alkanes before aromatics can be formed.

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TABLE 1

CATALYSTS CHARACTERIZATION

| | <u>CO/Pd</u> | <u>Crystallite Size (Å)</u> | |
|------------------------|--------------|-----------------------------|------------|
| | | <u>CO Chemisorption</u> | <u>XRD</u> |
| 2% Pd/H-ZSM5 | 0.128 | 76 | 152Å |
| 2% Pd/Na-ZSM5 | 0.128 | 76 | 143Å |
| 2% Pd/La-ZSM5 | 0.029 | 425 | |
| 2% Pd/SiO ₂ | 0.028 | 441 | |

ZSM5 SiO₂/Al₂O₃ = 36.7, 76% crystallinity

Na content below 20 ppm

SiO₂ Cabot EH-5, fumed silica

TABLE 2

Electron Binding Energies
(ref. to the C1s line at 284.6 eV)

| | Si 2p | O 1s | C 1s | Pd 3d 5/2 | Pd 3d 3/2 | Na 1s | Al 2p | La 3d |
|---|-------|-------|-------|-----------|-----------|--------|-------|-------|
| Pd/SiO ₂ ground pellet | 103.3 | 532.3 | 284.6 | 335.0 | 340.0 | 1017.8 | -- | -- |
| Pd/SiO ₂ ground pellet 1 1/2, 3hr, 500°C | 103.7 | 532.7 | 284.6 | 334.5 | 340.0 | 1071.8 | -- | -- |
| Pd/NaZSM5 on In foil | 103.3 | 532.3 | 284.6 | 335.1 | 340.4 | | 74.6 | -- |
| Pd/NaZSM5 on In Foil | 103.3 | 532.5 | 284.6 | 335.3 | 340.6 | | 74.5 | -- |
| Pd/LaZSM5 on In Foil | 103.0 | 532.0 | 284.6 | 335.0 | 340.2 | | 74.2 | 834.7 |

TABLE 3

ATOMIC RATIOS

Si held constant to 1

ATOMIC PERCENT

| | Si | O | C | Pd | Na | Al | La | Si | O | C | Pd | Na | Al | La |
|--|----|------|------|------|------|------|-----|------|------|------|-----|------|-------|------|
| Pd/SiO ₂ -H grnd pellet | 1 | 2.20 | .069 | .004 | .001 | -- | -- | 30.5 | 67.1 | 2.1 | .13 | .03 | Trace | -0- |
| Pd/SiO ₂ -H grnd pellet 1 1/2, 500°C, 3hr | 1 | 2.04 | .127 | .005 | .051 | -- | -- | 31.0 | 63.3 | 3.9 | .15 | 1.57 | -0- | -0- |
| Pd/NaZ-H on In foil | 1 | 2.17 | .069 | .011 | .044 | .038 | -- | 30.0 | 65.2 | 2.1 | .33 | 1.31 | 1.14 | -0- |
| Pd/NaZ-1 on In foil | 1 | 2.13 | .070 | .012 | .054 | .037 | -- | 30.3 | 64.5 | 2.1 | .35 | 1.64 | 1.12 | -0- |
| Pd/LaZ-H | 1 | 3.19 | .38 | .03 | .03 | .07 | .53 | 19.1 | 60.9 | 7.20 | .60 | 0.61 | 1.33 | 10.2 |

Figure 1 Adsorbed CO on

Temp = 45°C
Press. = atm.
10% CO/N₂

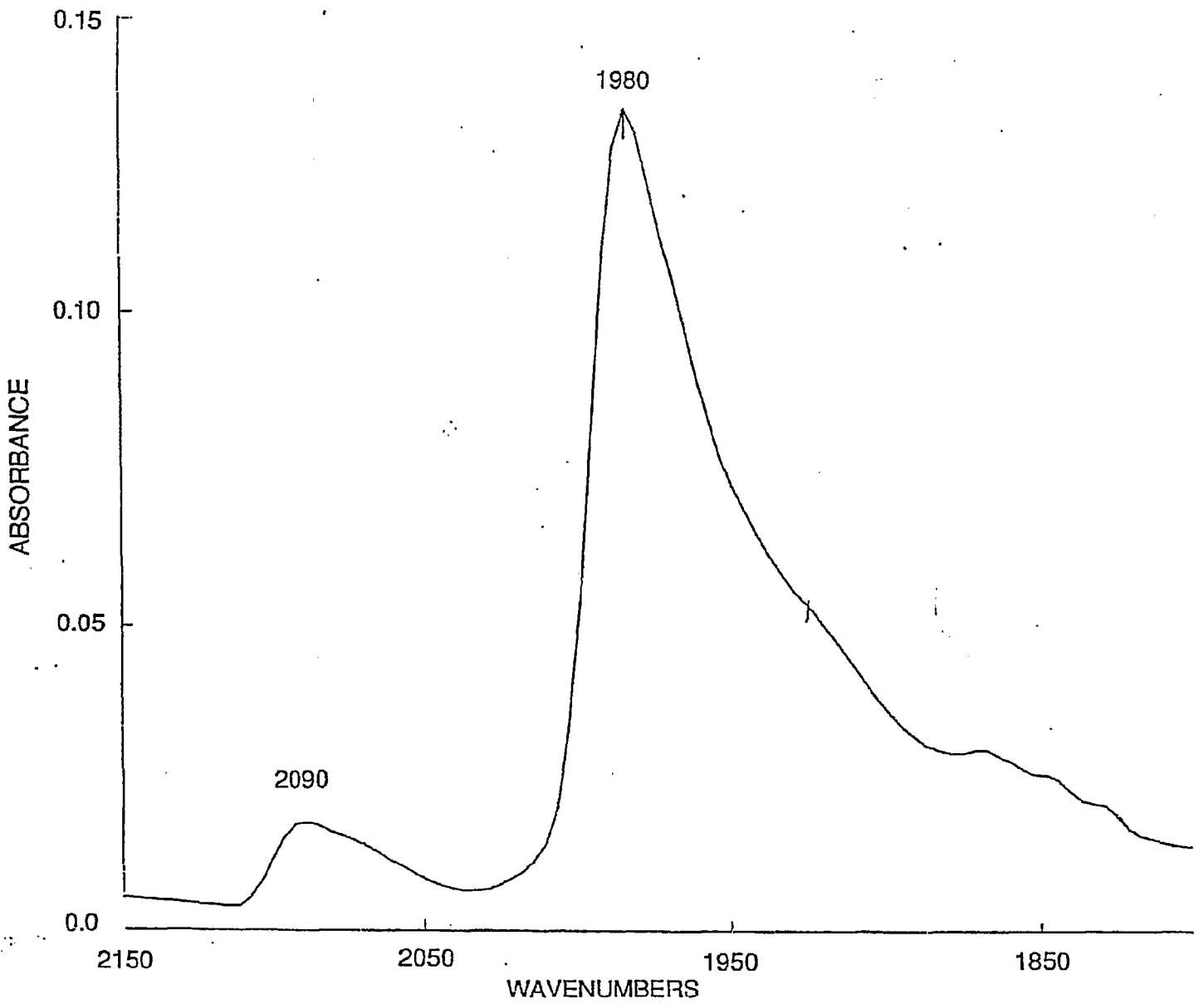


Figure 2 Yield vs: Time-on-Stream

2% Pd/La-ZSM5
Temp= 250°C
Press.= 250 psig
Flow Rate= 180 ml/min
H₂/CO= 2.0

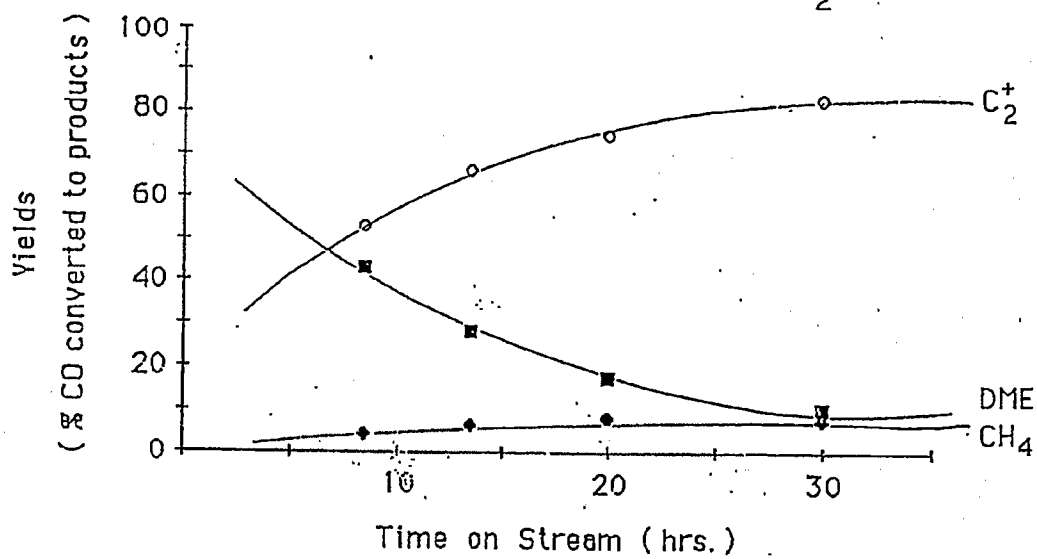


Figure 3 Effect of Temperature on Activity and Turnover Frequency

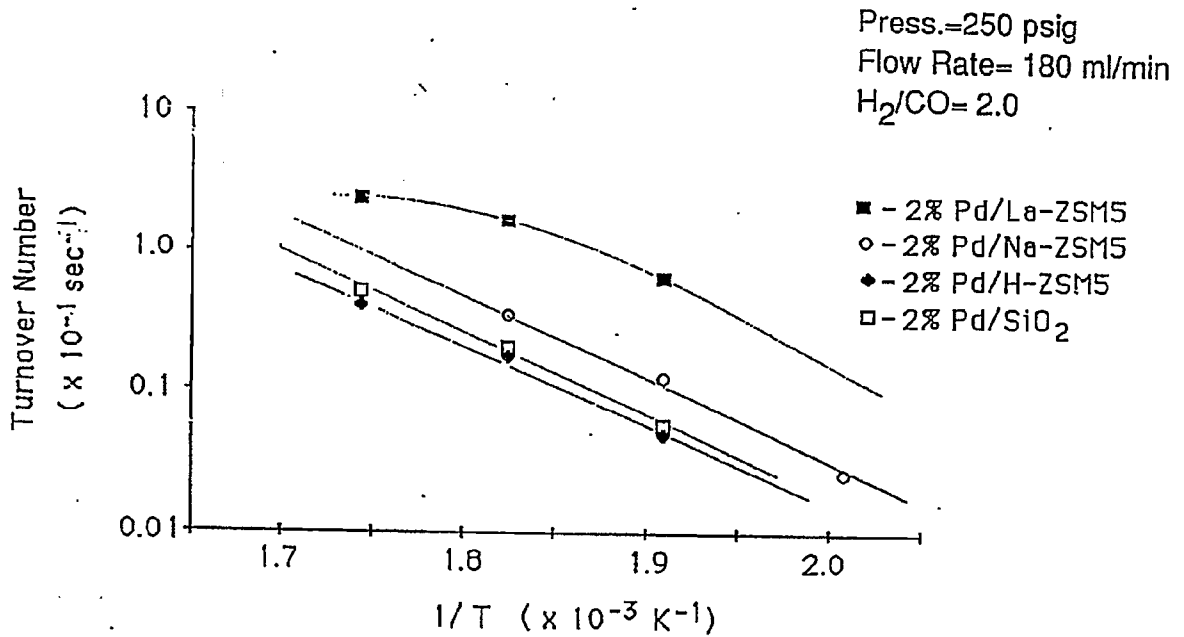
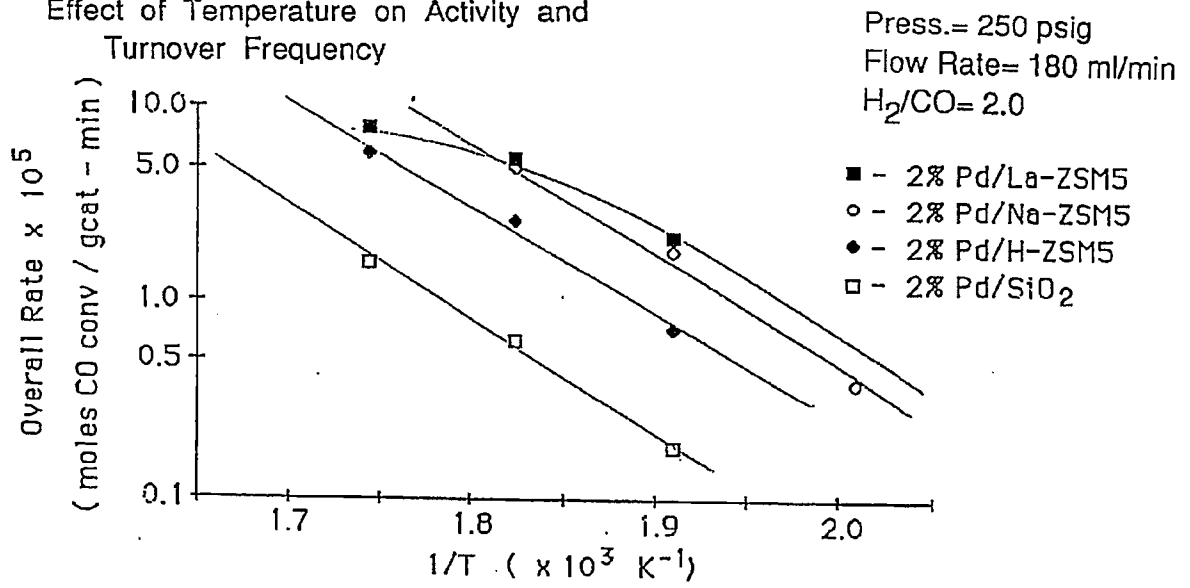
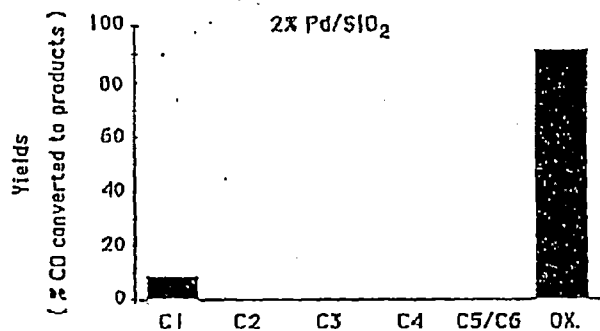
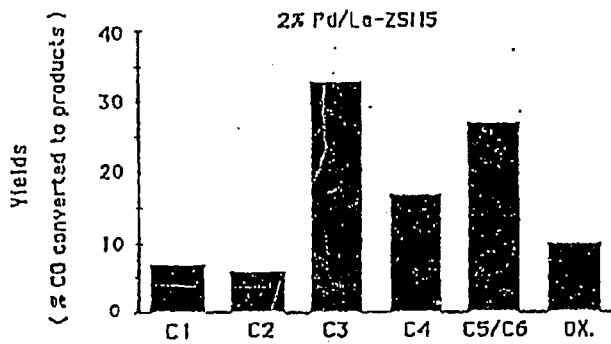
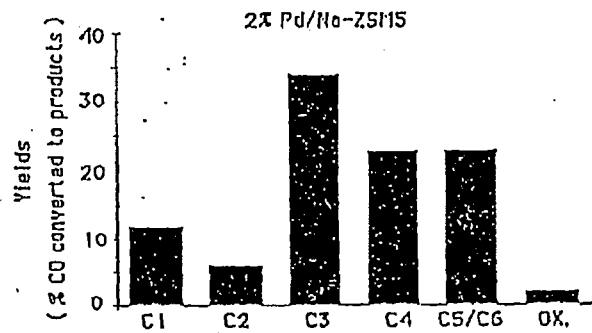
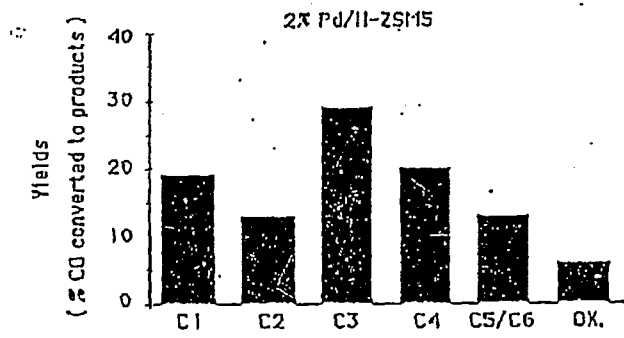


Figure 4. Product Distributions at Steady-State

Temp= 250 °C
 Press.= 250 psig
 Flow Rate= 180 ml/min
 H₂/CO= 2.0



∴ Figure 5 Product Yields vs. Temperature

Press.=250 psig
Flow Rate= 180 ml/min
 $H_2/CO= 2.0$

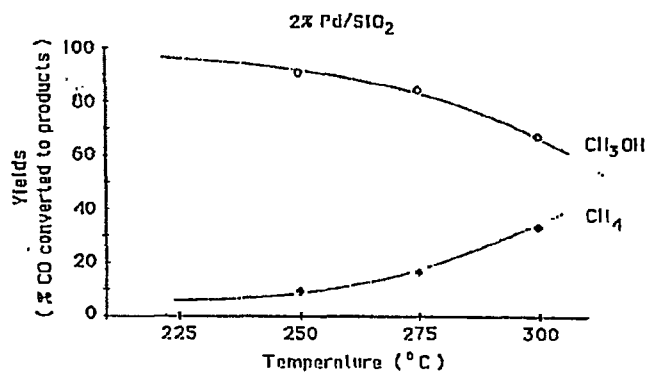
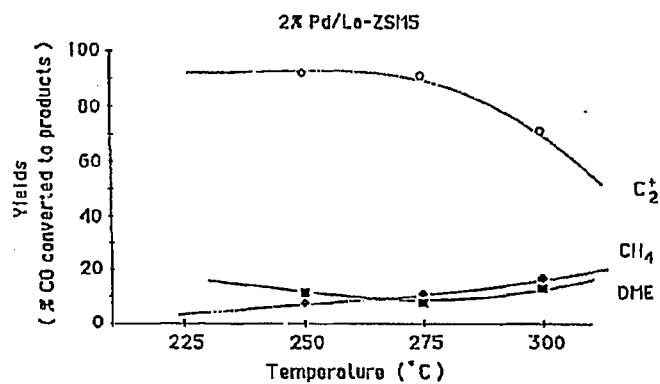
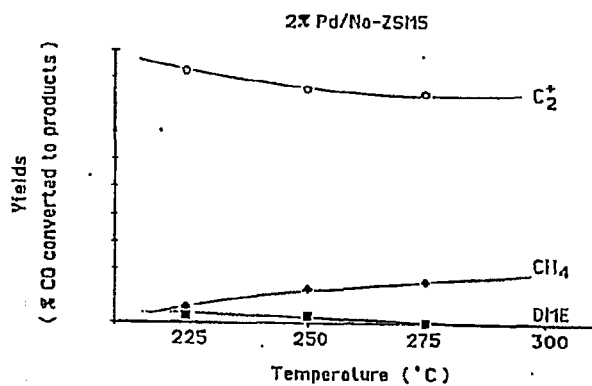
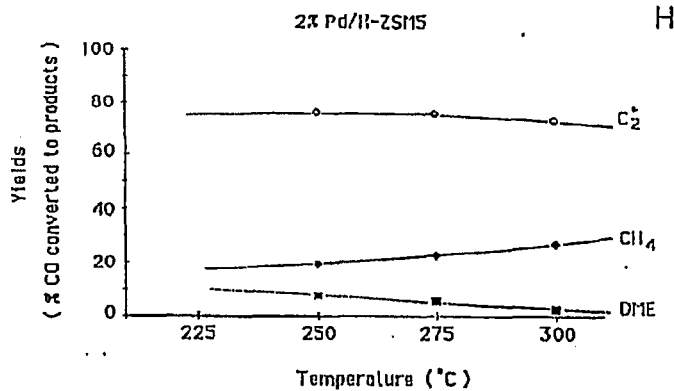


Figure 6 Effect of H_2/CO Ratio on Overall Activity

Temp=250 °C
Press.= 250 psig
Flow Rate= 180 ml/min

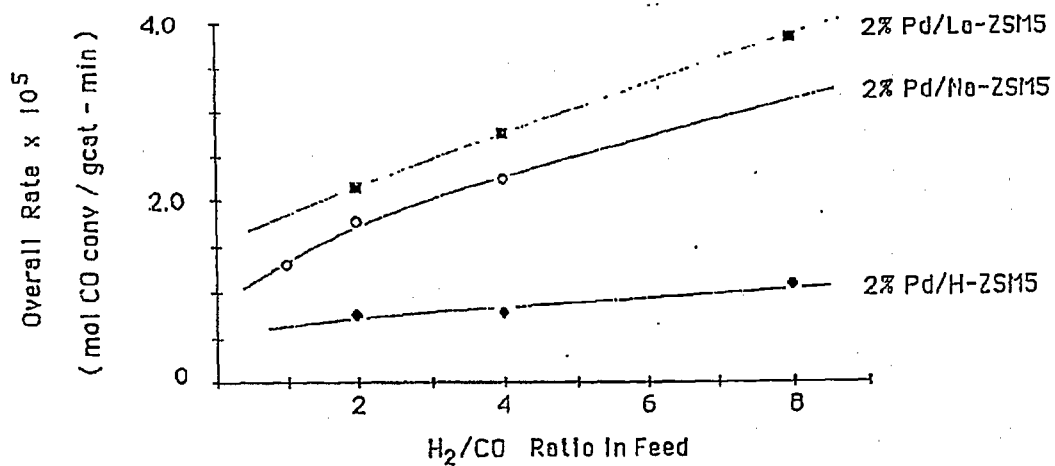


Figure 7 Effect of H_2/CO Ratio on Product Yields

Temp=250 °C
 Press.= 250 psig
 Flow Rate= 180 ml/min

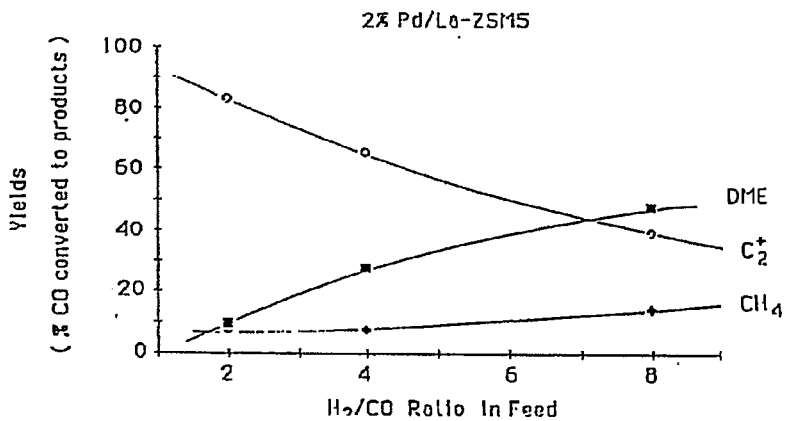
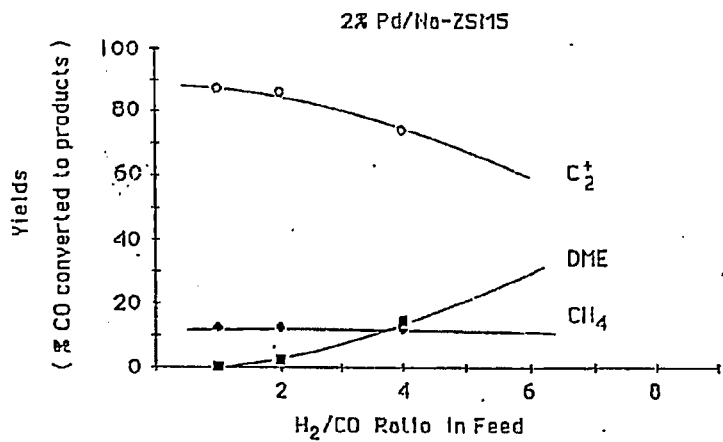
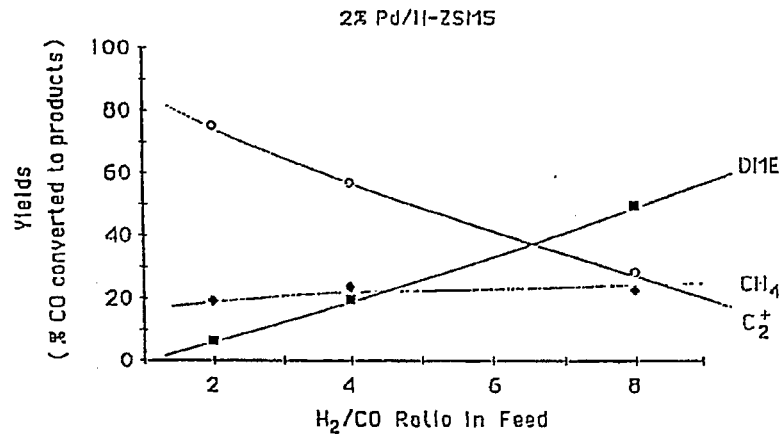


Figure 8 Product Distributions of Impregnated and Physically-Mixed Catalysts

Temp= 250 °C
Press.= 250 psig
Flow Rate= 180 ml/min
H₂/CO= 2.0

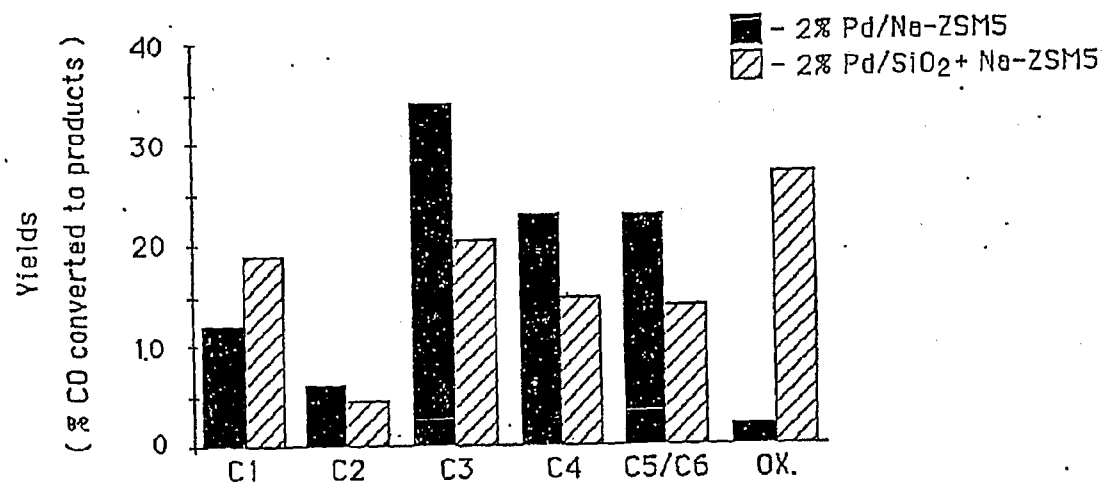


Figure 9

Effect of Flow Rate on Overall and DME
Production Rates

2% Pd/Na-ZSM5
Temp.= 250°C
Press.=250 psig
H₂/CO= 2.0

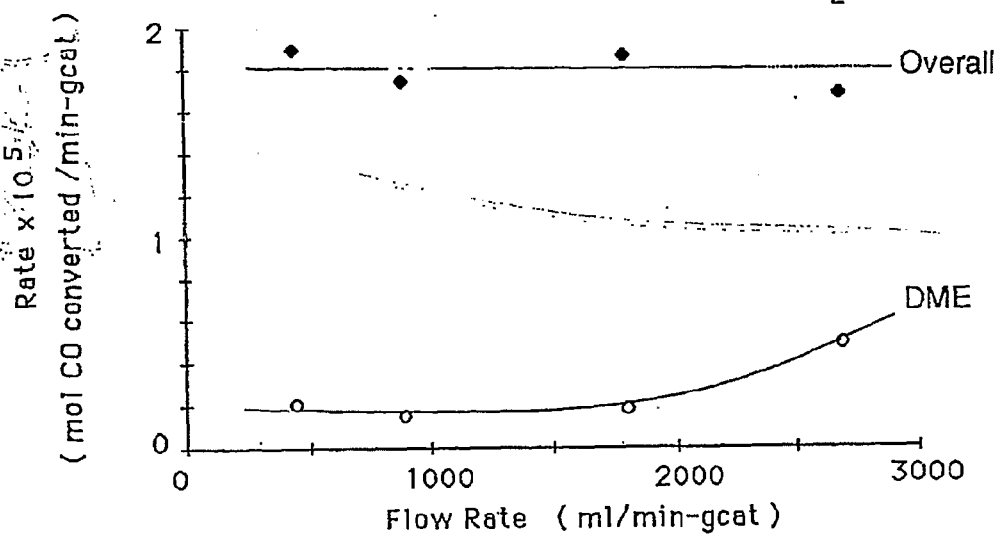


Figure 10 IR Spectra under Reaction Conditions

Temp = 250 °C
Press. = 250 psig
H₂/CO = 2.0

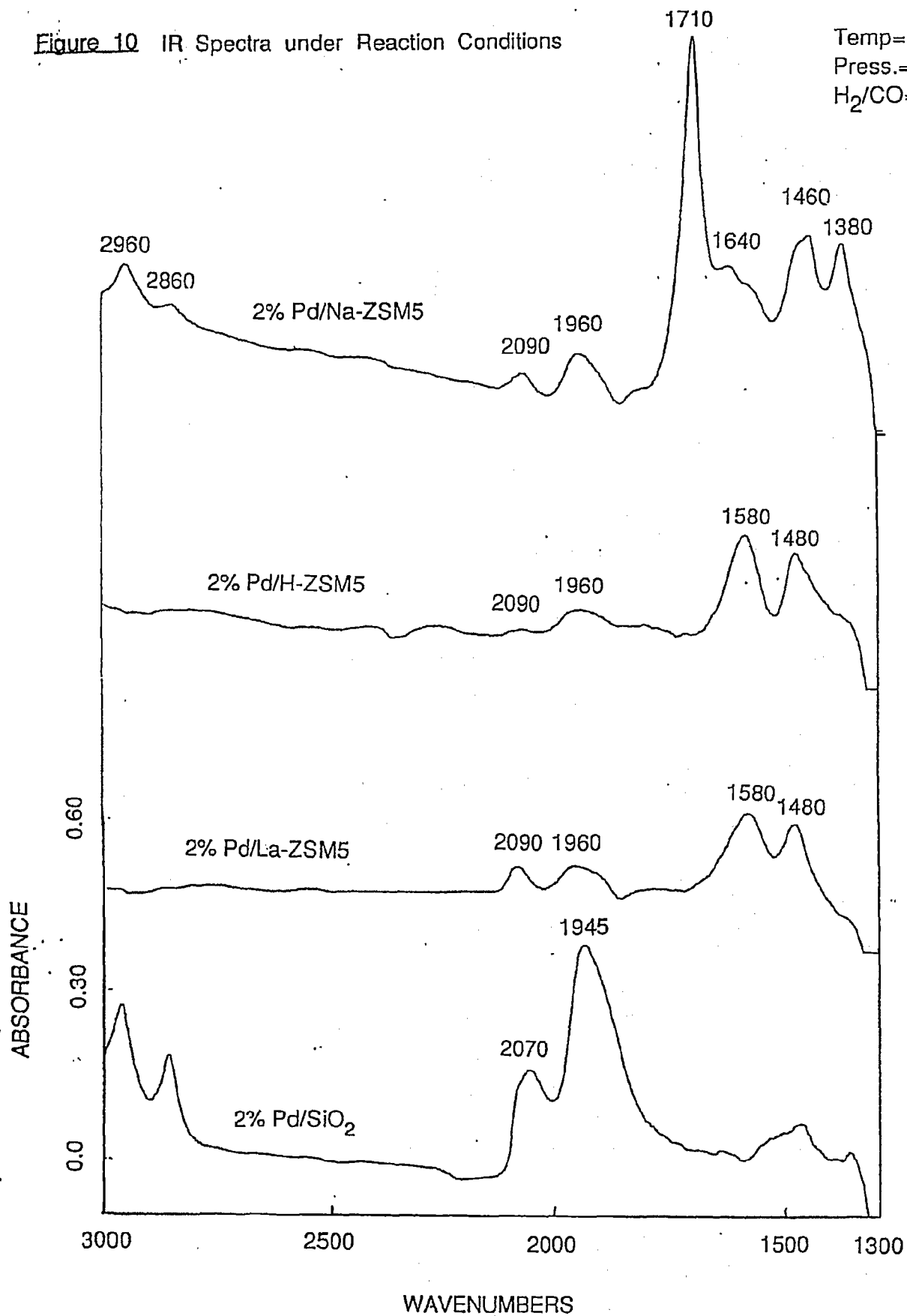


Figure 11
IR Spectra During Induction Period
over 2% Pd/Na-ZSM5

Temp = 250 °C
Press. = 250 psig
H₂/CO = 2.0

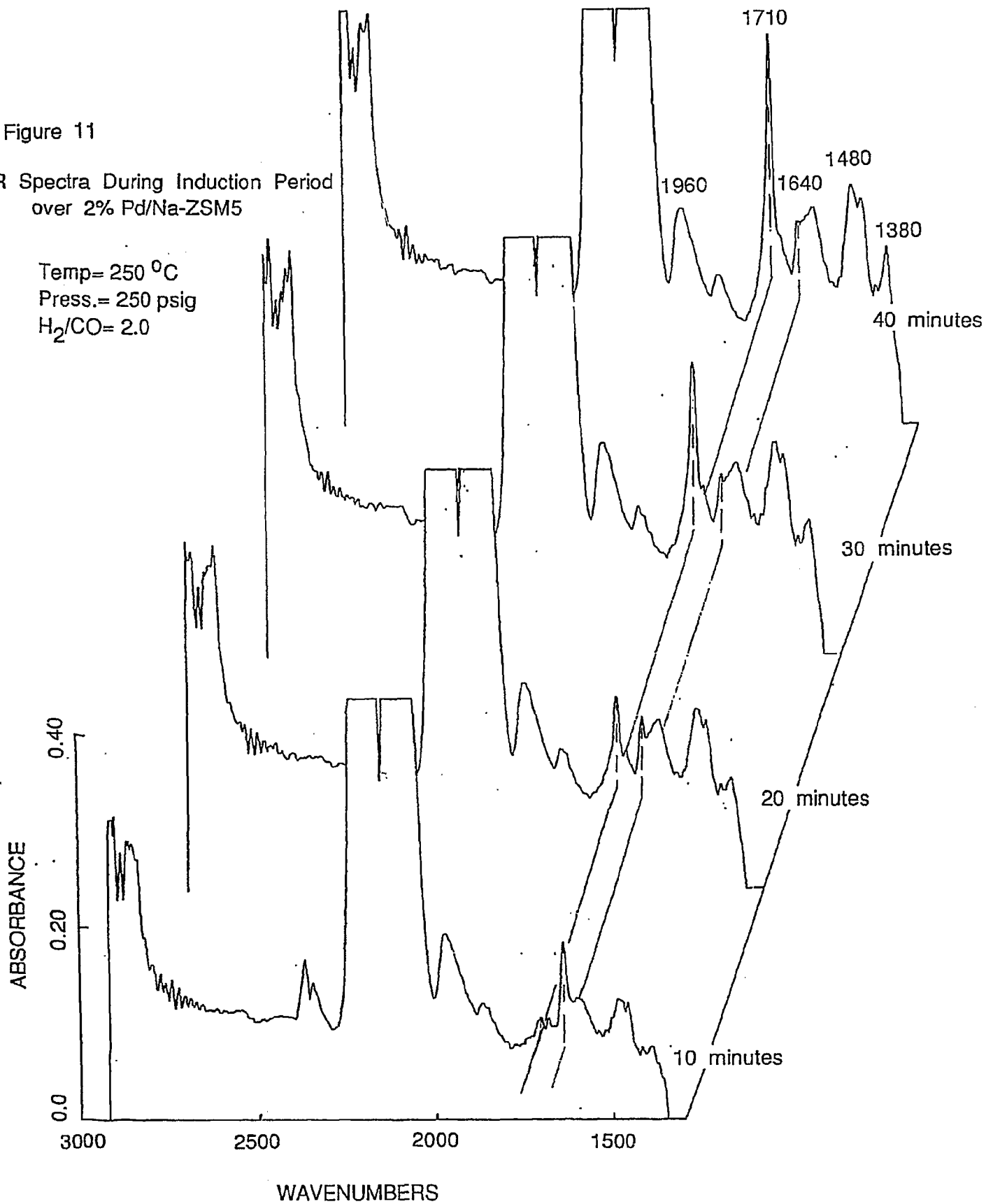


Figure 12 IR Spectra of 2% Pd/Na-ZSM5 During
Temperature-Programmed Reaction

Press. = 250 psig
 $H_2/CO = 2.0$

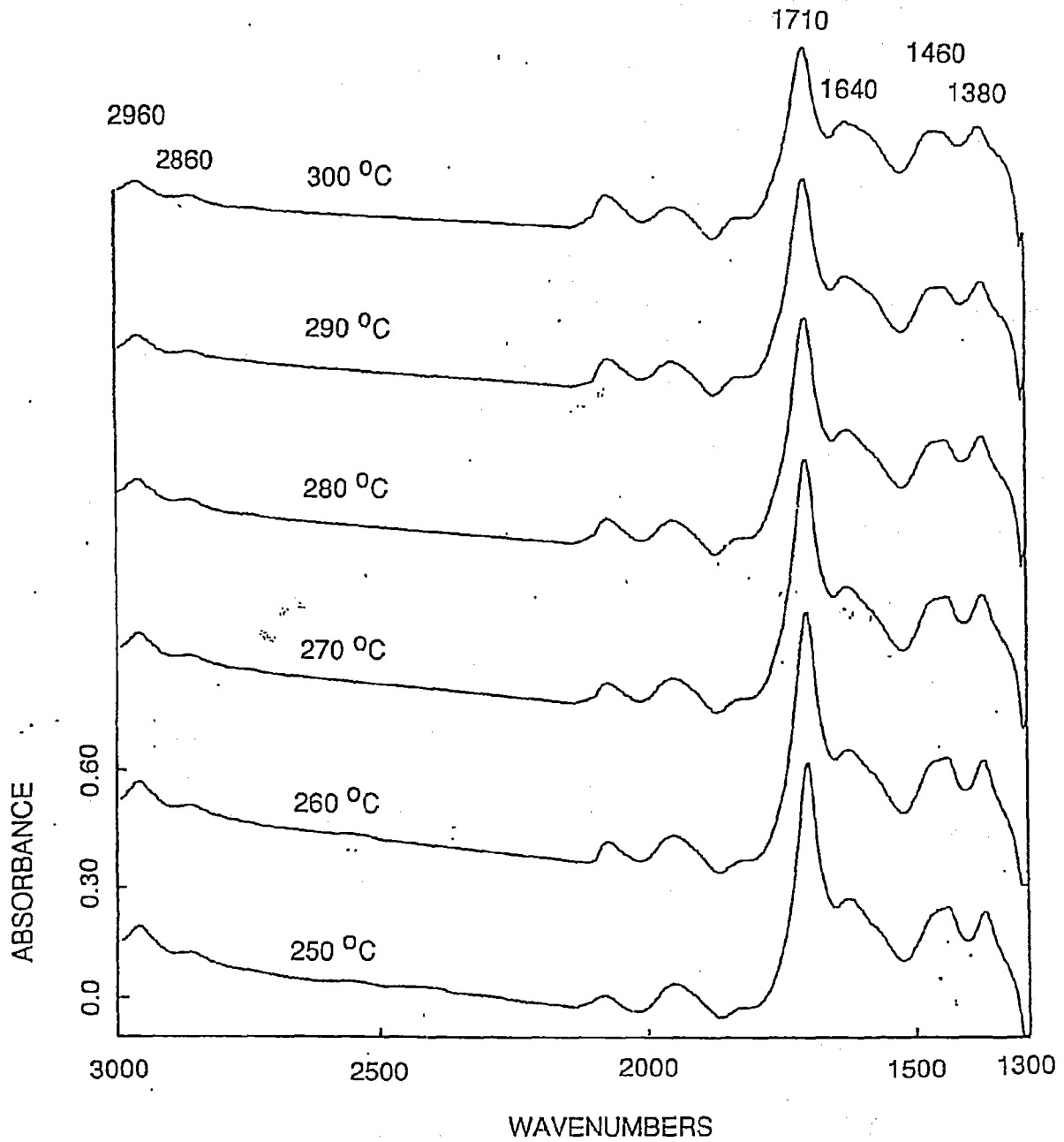


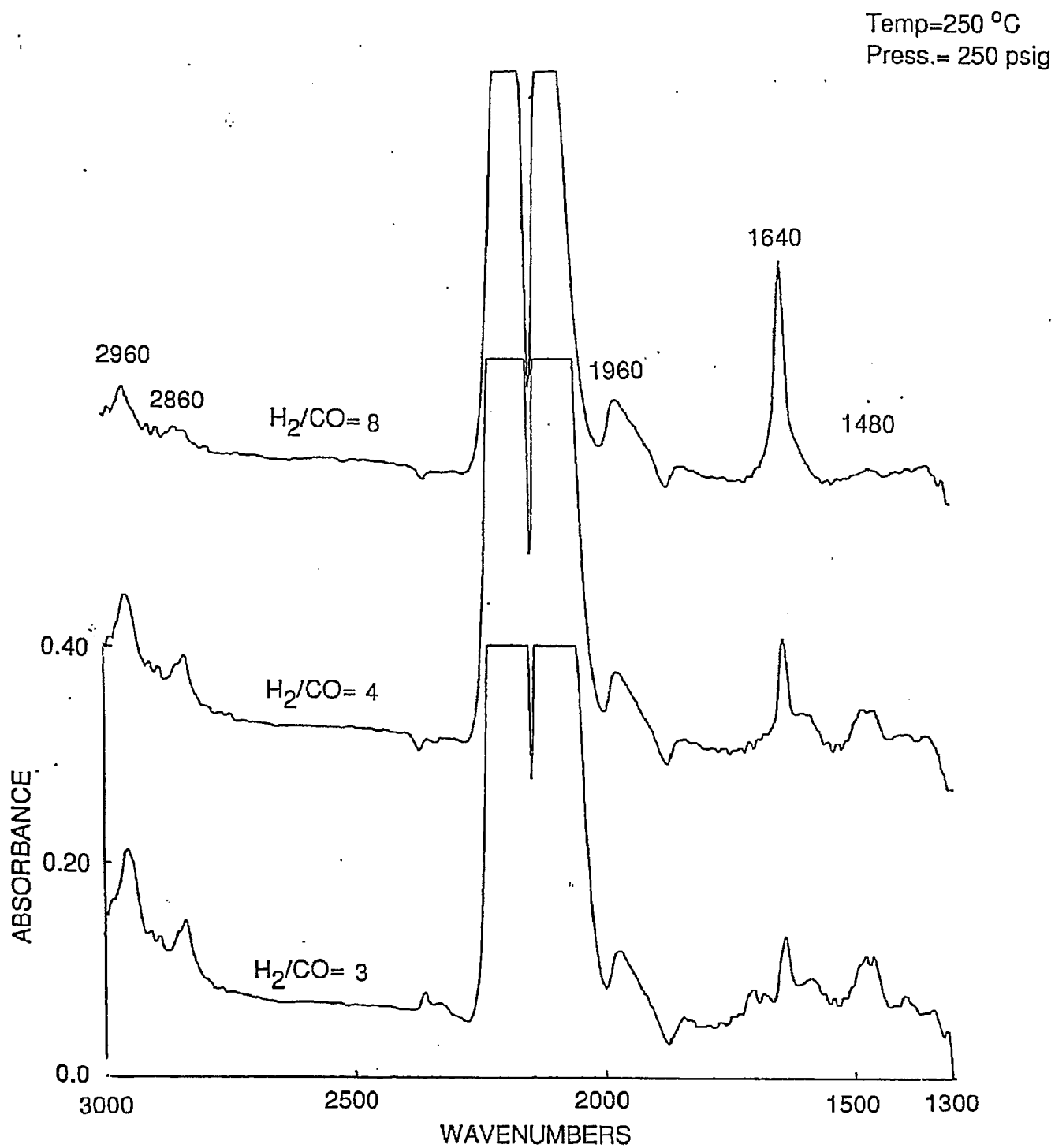
Figure 13 IR Spectra of 2% Pd/Na-ZSM5 under Various H₂/CO Ratios

Figure 14 IR Spectra of Depositions on Na-ZSM5 at 250 °C

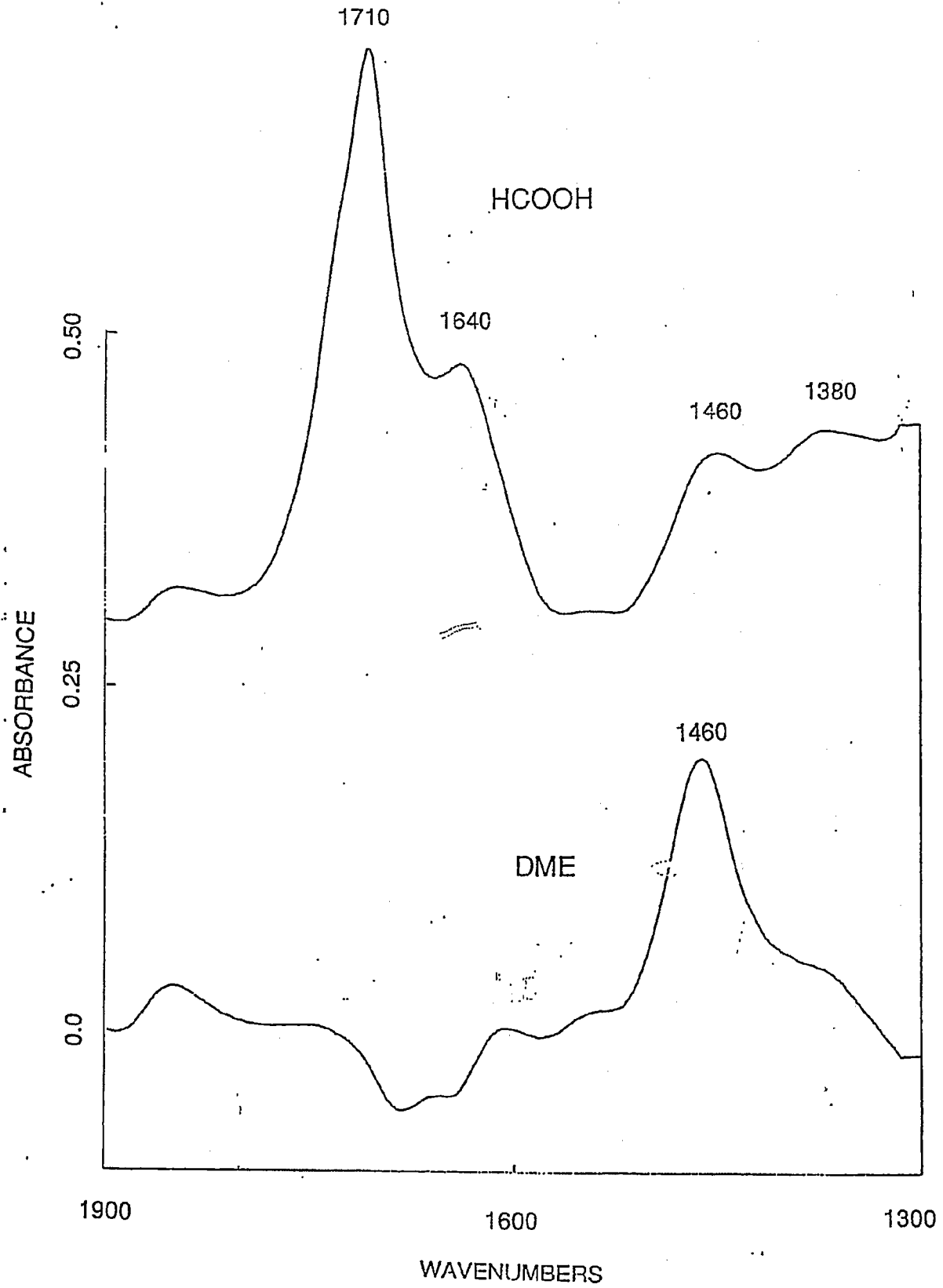
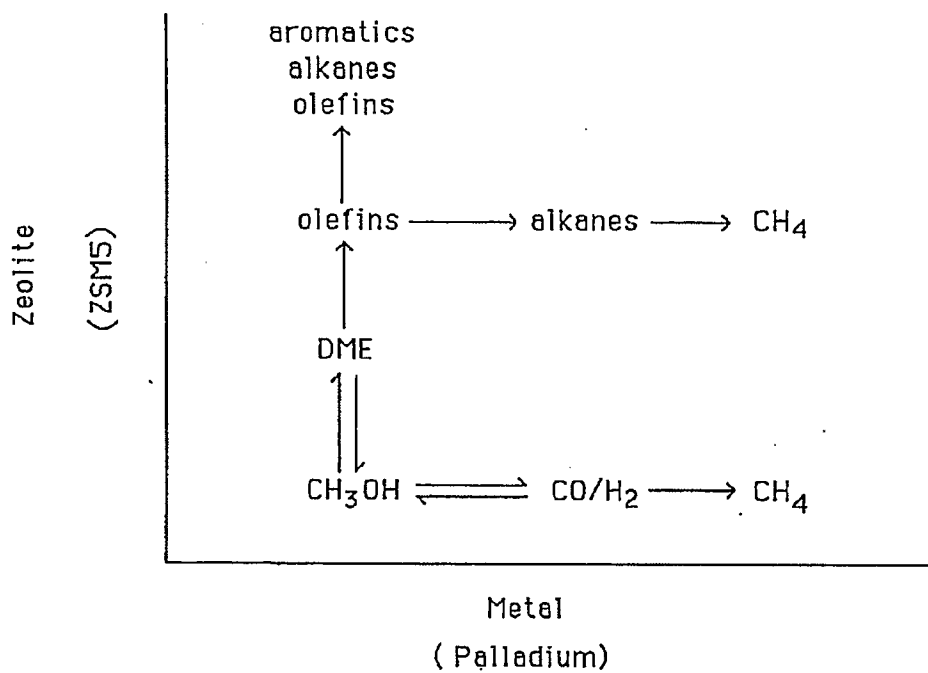


Figure 15

Reaction Pathway of Hydrocarbon Synthesis
over Pd/ZSM5

The rate of CO conversion to all products is added to find the overall rate. Turnover frequency is then determined by dividing the overall rate by the number of metal sites per gram of catalyst as determined by chemisorption.

$$\begin{aligned} \# \text{ metal sites} &= \left(\frac{\text{wt. metal}}{\text{gram catalyst}} \right) \left(\frac{1}{\text{MW Pd}} \right) \left(\frac{\# \text{ Pd sites}}{\text{mol Pd}} \right) \\ &= \left(\frac{.02 \text{ g Pd}}{\text{g cat.}} \right) \left(\frac{\text{mol Pd}}{106.4 \text{ g Pd}} \right) \left(\frac{.128 \text{ moles sites}}{\text{mol Pd}} \right) \\ &= 2.41 \times 10^{-5} \text{ mol sites/gcat} \end{aligned}$$

$$\therefore \text{ turnover freq.} = \frac{.737 \times 10^{-5} \frac{\text{mol Co conv}}{\text{g cat} \cdot \text{min}}}{2.41 \times 10^{-5} \text{ mol sites/gcat}} = .306/\text{min} = 5.10 \times 10^{-2}/\text{sec}$$

Yields are calculated by dividing individual rates by the overall rates.

$$\begin{aligned} \text{C}_3\text{H}_8 \text{ rate} &= .215 \times 10^{-5} \\ \text{overall rate} &= .737 \times 10^{-5} \\ \text{yield C}_3\text{H}_8 &= \frac{.215 \times 10^{-5}}{.737 \times 10^{-5}} = 29.1\% \end{aligned}$$

Chemisorption

To determine dispersion, CO was pulsed through a catalyst bed (typically 1.0 g) until the CO peaks detected by TC cell were the same size. Each CO pulse contained 135.4 μl CO. Dispersion, defined as the ratio of surface Pd sites to total Pd atoms, was calculated assuming that #CO chemisorbed = #Pd Surface sites.

Given : 4.38 CO pulses to saturate a 1.0 g sample of 2% Pd/H-ZSM5

$$\begin{aligned} \# \text{ Pd sites} &= (4.39 \text{ pulses})(135.4 \mu\text{l CO/pulse}) \left(\frac{1 \text{ atm}}{(82050 \frac{\text{atm} \mu\text{l}}{\text{K mol}})(300^\circ\text{K})} \right) \\ &= 2.41 \times 10^{-5} \text{ mol Pd surf. atoms} \end{aligned}$$

$$\text{Total Pd atoms} = (1.0 \text{ g cat}) \left(\frac{.02 \text{ g Pd}}{\text{g cat}} \right) \left(\frac{1 \text{ mol Pd atoms}}{106.4 \text{ g Pd}} \right) = 1.88 \times 10^{-4} \text{ mol Pd atoms}$$

Assuming the Pd crystallites are present on the support surface as hemispheres, the total surface area of metal can be written

$$\text{surf. area Pd} = (\text{number cryst.}) \pi (\text{cryst. diameter})^2/2$$

The volume of these crystallites can be expressed as

$$V = (\text{number cryst.}) \pi (\text{cryst. diameter})^3/12$$

Dividing volume by surface area yields average crystallite diameter

$$\text{cryst. diameter} = 6 \left(\frac{\text{volume Pd}}{\text{surf. area Pd}} \right)$$

Volume can be calculated by employing the bulk density

$$\begin{aligned} V &= (.02 \text{ g Pd/gcat})(1.0 \text{ gcat})/(12.0 \text{ g Pd/cc}) \\ &= 1.67 \times 10^{-3} \text{ cc Pd} \end{aligned}$$

Assuming that one CO chemisorbs for each Pd surface atom

$$\begin{aligned} \text{Surf. Area} &= (2.41 \times 10^{-5} \text{ mol Pd surf. atoms})(6.02 \times 10^{23} \frac{\text{atoms}}{\text{mol}}) \left(\frac{1 \text{ cm}^2}{1.1 \times 10^{15} \text{ Pd atoms}} \right) \\ &= 1.39 \times 10^4 \text{ cm}^2 \end{aligned}$$

$$\therefore \text{cryst. diameter} = 6 \left(\frac{1.67 \times 10^{-3} \text{ cm}^3}{1.319 \times 10^4 \text{ cm}^2} \right) = 75.8 \text{ \AA}$$

XRD

The scherrer equation was used to calculate Pd crystallite size from the Pd (111) peak at $2\theta=40.2^\circ$ the equation

$$d = .94 \lambda/B \cos \theta$$

requires a corrected value for the peak broadening. Assuming an instrument broadening of $.330^\circ$ of 2θ , B is found using $B = (B_{\text{exper.}}^2 - B_{\text{inst.}}^2)^{1/2}$

Given an experimental broadening of $2\theta=0.67^\circ$ for Pd/H-ZSM5

$$\begin{aligned} B &= ((.67)^2 - (.330)^2)^{1/2} = .583^\circ \text{ of } 2\theta \\ &= .0102 \text{ radians} \end{aligned}$$

$$\lambda = 1.542 \text{ \AA}$$

$$\cos \theta = \cos (20.1^\circ) = .939$$

$$\therefore d = .94 (1.542 \text{ \AA})/ (.0102)(.939) = 152 \text{ \AA}$$

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Data for Fig. 2

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 250 C PRESSURE= 250 PSIG H2/CO= 2.0
 FLOW RATE= 180 ML/MIN 9.0 HOURS ON STREAM

RATE= 0.164E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.14 %

| PRODUCT | RATE | YIELD |
|---------|-----------|--------|
| C1 | 0.639E-06 | 3.9 % |
| C2 | 0.113E-05 | 6.9 % |
| C3 | 0.406E-05 | 24.8 % |
| C4 | 0.100E-05 | 6.1 % |
| C5 | 0.195E-05 | 11.9 % |
| CH3OH | 0.585E-06 | 3.6 % |
| CH3OCH3 | 0.702E-05 | 42.8 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 250 C PRESSURE= 250 PSIG H2/CO= 2.0
 FLOW RATE= 180 ML/MIN 14.0 HOURS ON STREAM

RATE= 0.157E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.13 %

| PRODUCT | RATE | YIELD |
|---------|-----------|--------|
| C1 | 0.506E-06 | 5.7 % |
| C2 | 0.130E-05 | 8.1 % |
| C3 | 0.514E-05 | 32.2 % |
| C4 | 0.162E-05 | 10.2 % |
| C5 | 0.244E-05 | 15.3 % |
| CH3OH | 0.000E+00 | 0.0 % |
| CH3OCH3 | 0.433E-05 | 28.4 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 250 C PRESSURE= 250 PSIG H2/CO= 2.0
 FLOW RATE= 180 ML/MIN 20.0 HOURS ON STREAM

RATE= 0.176E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.14 %

| PRODUCT | RATE | YIELD |
|---------|-----------|--------|
| C1 | 0.133E-05 | 7.6 % |
| C2 | 0.140E-05 | 8.0 % |
| C3 | 0.570E-05 | 33.6 % |
| C4 | 0.239E-05 | 14.8 % |
| C5 | 0.329E-05 | 18.5 % |
| CH3OH | 0.000E+00 | 0.0 % |
| CH3OCH3 | 0.307E-05 | 17.5 % |

Fig. 2 (cont.)

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 180 ML/MIN 30.0 HOURS ON STREAM

RATE= 0.213E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.17 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.149E-05 | 7.0 % |
| C2 | 0.140E-05 | 6.6 % |
| C3 | 0.713E-05 | 33.5 % |
| C4 | 0.351E-05 | 16.5 % |
| C5 | 0.570E-05 | 26.8 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.205E-05 | 9.6 % |

Data for Fig. 3, 4, 5

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 32.0 HOURS ON STREAM

RATE= 0.737E-05 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.03 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.139E-05 | 18.8 % |
| C2 | 0.918E-06 | 12.5 % |
| C3 | 0.215E-05 | 29.1 % |
| C4 | 0.150E-05 | 20.4 % |
| C5 | 0.976E-06 | 13.2 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.438E-06 | 6.0 % |

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 275 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 35.0 HOURS ON STREAM

RATE= 0.259E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.11 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.575E-05 | 22.2 % |
| C2 | 0.313E-05 | 12.1 % |
| C3 | 0.521E-05 | 20.1 % |
| C4 | 0.702E-05 | 27.1 % |
| C5 | 0.391E-05 | 15.1 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.877E-06 | 3.4 % |

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 300 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 44.0 HOURS ON STREAM

RATE= 0.585E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.24 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.158E-04 | 27.0 % |
| C2 | 0.648E-05 | 11.1 % |
| C3 | 0.138E-04 | 23.6 % |
| C4 | 0.140E-04 | 24.0 % |
| C5 | 0.781E-05 | 13.4 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.585E-06 | 1.0 % |

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Fig. 3, 4, 5 (cont.)

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
TEMP= 225 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 180 ML/MIN 29.0 HOURS ON STREAM

RATE= 0.378E-05 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.03 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.213E-06 | 5.6 % |
| C2 | 0.135E-06 | 3.6 % |
| C3 | 0.882E-06 | 23.3 % |
| C4 | 0.155E-05 | 40.8 % |
| C5 | 0.936E-06 | 24.7 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.730E-07 | 1.9 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 180 ML/MIN 11.0 HOURS ON STREAM

RATE= 0.177E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.15 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.213E-05 | 12.0 % |
| C2 | 0.108E-05 | 6.1 % |
| C3 | 0.613E-05 | 34.6 % |
| C4 | 0.401E-05 | 22.6 % |
| C5 | 0.407E-05 | 23.0 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.292E-06 | 1.7 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
TEMP= 275 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 180 ML/MIN 35.0 HOURS ON STREAM

RATE= 0.490E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.40 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.725E-05 | 14.8 % |
| C2 | 0.389E-05 | 7.9 % |
| C3 | 0.138E-04 | 28.2 % |
| C4 | 0.110E-04 | 22.5 % |
| C5 | 0.130E-04 | 26.6 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.000E+00 | 0.0 % |

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Fig. 3, 4, 5 (cont.)

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 40.0 HOURS ON STREAM

RATE= 0.214E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.18 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.149E-05 | 7.0 % |
| C2 | 0.130E-05 | 6.0 % |
| C3 | 0.670E-05 | 32.2 % |
| C4 | 0.401E-05 | 18.7 % |
| C5 | 0.570E-05 | 26.6 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.205E-05 | 9.5 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 275 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 43.0 HOURS ON STREAM

RATE= 0.550E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.45 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.573E-05 | 10.5 % |
| C2 | 0.367E-05 | 6.7 % |
| C3 | 0.172E-04 | 34.9 % |
| C4 | 0.986E-05 | 17.9 % |
| C5 | 0.130E-04 | 23.7 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.351E-05 | 6.4 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
 TEMP= 300 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 46.0 HOURS ON STREAM

RATE= 0.791E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.65 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.132E-04 | 16.7 % |
| C2 | 0.470E-05 | 8.5 % |
| C3 | 0.230E-04 | 29.1 % |
| C4 | 0.120E-04 | 15.2 % |
| C5 | 0.137E-04 | 17.3 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.105E-04 | 13.3 % |

Fig. 3, 4, 5 (cont.)

200.0 MG OF 2% Pd/SiO₂ STARTED 3/15/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 14.0 HOURS ON STREAM

RATE= 0.175E-05 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.02 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.160E-06 | 9.2 % |
| C2 | 0.000E+00 | 0.0 % |
| C3 | 0.000E+00 | 0.0 % |
| C4 | 0.000E+00 | 0.0 % |
| C5 | 0.000E+00 | 0.0 % |
| CH ₃ OH | 0.159E-05 | 90.8 % |
| CH ₃ OCH ₃ | 0.000E+00 | 0.0 % |

200.0 MG OF 2% Pd/SiO₂ STARTED 3/15/86
 TEMP= 250 C PRESSURE= 275 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 20.0 HOURS ON STREAM

RATE= 0.635E-05 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.05 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.799E-06 | 12.6 % |
| C2 | 0.189E-06 | 3.0 % |
| C3 | 0.000E+00 | 0.0 % |
| C4 | 0.000E+00 | 0.0 % |
| C5 | 0.000E+00 | 0.0 % |
| CH ₃ OH | 0.537E-05 | 84.4 % |
| CH ₃ OCH ₃ | 0.000E+00 | 0.0 % |

200.0 MG OF 2% Pd/SiO₂ STARTED 3/15/86
 TEMP= 300 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 24.0 HOURS ON STREAM

RATE= 0.160E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.13 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.416E-05 | 26.0 % |
| C2 | 0.130E-05 | 8.1 % |
| C3 | 0.000E+00 | 0.0 % |
| C4 | 0.000E+00 | 0.0 % |
| C5 | 0.000E+00 | 0.0 % |
| CH ₃ OH | 0.105E-04 | 65.9 % |
| CH ₃ OCH ₃ | 0.000E+00 | 0.0 % |

Data for Fig. 6, 7

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 32.0 HOURS ON STREAM

RATE= 0.737E-05 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.03 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.139E-05 | 18.8 % |
| C2 | 0.918E-06 | 12.5 % |
| C3 | 0.215E-05 | 29.1 % |
| C4 | 0.150E-05 | 20.4 % |
| C5 | 0.976E-06 | 13.2 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.438E-06 | 5.0 % |

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 4.0
 FLOW RATE= 180 ML/MIN 28.0 HOURS ON STREAM

RATE= 0.751E-05 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.05 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.176E-05 | 23.4 % |
| C2 | 0.756E-06 | 10.1 % |
| C3 | 0.138E-05 | 18.4 % |
| C4 | 0.134E-05 | 17.8 % |
| C5 | 0.814E-06 | 10.8 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.146E-05 | 19.5 % |

200.0 MG OF 2% Pd/H-ZSM5 STARTED 3/17/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 8.0
 FLOW RATE= 180 ML/MIN 24.0 HOURS ON STREAM

RATE= 0.106E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.13 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.232E-05 | 21.8 % |
| C2 | 0.756E-06 | 7.1 % |
| C3 | 0.115E-05 | 10.8 % |
| C4 | 0.752E-06 | 7.1 % |
| C5 | 0.407E-06 | 3.8 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.526E-05 | 49.4 % |

Fig. 6, 7 (cont.)

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 11.0 HOURS ON STREAM

RATE= 0.177E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.15 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.213E-05 | 12.0 % |
| C2 | 0.108E-05 | 6.1 % |
| C3 | 0.613E-05 | 34.6 % |
| C4 | 0.401E-05 | 22.6 % |
| C5 | 0.407E-05 | 23.0 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.272E-06 | 1.7 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 4.0
 FLOW RATE= 180 ML/MIN 9.0 HOURS ON STREAM

RATE= 0.222E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.30 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.256E-05 | 11.5 % |
| C2 | 0.130E-05 | 5.8 % |
| C3 | 0.675E-05 | 30.4 % |
| C4 | 0.443E-05 | 19.9 % |
| C5 | 0.399E-05 | 17.9 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.322E-05 | 14.5 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 3/9/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 1.0
 FLOW RATE= 180 ML/MIN 13.0 HOURS ON STREAM

RATE= 0.130E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.07 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.160E-05 | 12.3 % |
| C2 | 0.702E-06 | 5.4 % |
| C3 | 0.330E-05 | 25.4 % |
| C4 | 0.334E-05 | 25.7 % |
| C5 | 0.407E-05 | 31.3 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.000E+00 | 0.0 % |

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Fig. 6, 7 (cont.)

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 180 ML/MIN 30.0 HOURS ON STREAM

RATE= 0.213E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.17 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.149E-05 | 7.0 % |
| C2 | 0.140E-05 | 6.6 % |
| C3 | 0.713E-05 | 33.5 % |
| C4 | 0.351E-05 | 16.5 % |
| C5 | 0.570E-05 | 26.8 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.205E-05 | 9.6 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 4.0
FLOW RATE= 180 ML/MIN 34.0 HOURS ON STREAM

RATE= 0.274E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.38 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.192E-05 | 7.0 % |
| C2 | 0.151E-05 | 5.5 % |
| C3 | 0.736E-05 | 26.8 % |
| C4 | 0.401E-05 | 14.6 % |
| C5 | 0.504E-05 | 18.4 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.760E-05 | 27.7 % |

200.0 MG OF 2% Pd/La-ZSM5 STARTED 3/20/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 8.0
FLOW RATE= 180 ML/MIN 37.0 HOURS ON STREAM

RATE= 0.323E-04 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.94 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.533E-05 | 13.9 % |
| C2 | 0.173E-05 | 4.5 % |
| C3 | 0.491E-05 | 12.8 % |
| C4 | 0.347E-05 | 9.6 % |
| C5 | 0.456E-05 | 11.9 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.181E-04 | 47.3 % |

Data for Fig. 8

200.0 MG. OF 2% Pd/SiO₂+Na⁺-ZSM5 STARTED 5/14/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOWRATE= 180 ML/MIN 9.0 HOURS ON STREAM

RATE= 0.713E-05 MOLES CO CONVERTED/MIN-GCAT
CONVERSION= 0.06 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.139E-05 | 19.4 % |
| C2 | 0.324E-06 | 4.5 % |
| C3 | 0.146E-05 | 20.4 % |
| C4 | 0.109E-05 | 15.2 % |
| C5 | 0.976E-06 | 13.7 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.190E-05 | 26.7 % |

Data for Fig. 9

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 5/14/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 90 ML/MIN 21.0 HOURS ON STREAM

RATE= 0.189E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.31 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.272E-05 | 14.4 % |
| C2 | 0.140E-05 | 7.4 % |
| C3 | 0.583E-05 | 30.8 % |
| C4 | 0.301E-05 | 15.9 % |
| C5 | 0.391E-05 | 20.7 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.205E-05 | 10.8 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 5/14/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 180 ML/MIN 24.0 HOURS ON STREAM

RATE= 0.174E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.14 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.277E-05 | 15.9 % |
| C2 | 0.108E-05 | 6.2 % |
| C3 | 0.583E-05 | 33.5 % |
| C4 | 0.334E-05 | 19.2 % |
| C5 | 0.293E-05 | 16.8 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.146E-05 | 8.4 % |

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 5/14/86
 TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
 FLOW RATE= 360 ML/MIN 27.0 HOURS ON STREAM

RATE= 0.186E-04 MOLES CO CONVERTED/MIN-GCAT
 CONVERSION= 0.08 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.341E-05 | 18.3 % |
| C2 | 0.130E-05 | 7.0 % |
| C3 | 0.491E-05 | 26.4 % |
| C4 | 0.334E-05 | 17.9 % |
| C5 | 0.391E-05 | 21.0 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.175E-05 | 9.4 % |

Fig. 9, (cont.)

200.0 MG OF 2% Pd/Na-ZSM5 STARTED 5/14/86
TEMP= 250 C PRESSURE= 250 PSIG H₂/CO= 2.0
FLOW RATE= 540 ML/MIN 30.0 HOURS ON STREAM

RATE= 0.167E-05 MOLES CO CONVERTED/MIN-CAT
CONVERSION= 0.05 %

| PRODUCT | RATE | YIELD |
|----------------------------------|-----------|--------|
| C1 | 0.368E-05 | 22.0 % |
| C2 | 0.113E-05 | 6.8 % |
| C3 | 0.414E-05 | 24.7 % |
| C4 | 0.150E-05 | 9.0 % |
| C5 | 0.146E-05 | 8.7 % |
| CH ₃ OH | 0.000E+00 | 0.0 % |
| CH ₃ OCH ₃ | 0.482E-05 | 28.8 % |

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