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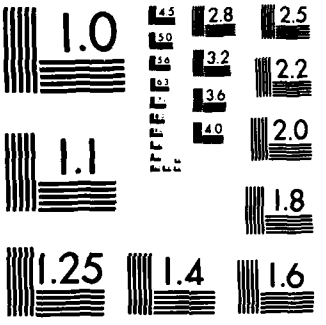

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An Infrared Study of the Hydrogenation of Carbon Dioxide on Supported Rhodium Catalysts

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ABSTRACT

An infrared study of the methanation of CO_2 on supported Rh catalysts has been performed. This reaction has been shown to occur over these catalysts with higher turnover frequency at a given temperature and Rh loading than does the methanation of CO. A support effect has been demonstrated for the reaction over the supported Rh catalysts (TiO_2 > Al_2O_3 > SiO_2 in reactivity). A key surface intermediate during the methanation reaction is a carbonyl hydride species, as evidenced by a prominent infrared band in the 2020 -2040 cm^{-1} region which shifts by 5-10 cm^{-1} when D_2 is substituted for H_2 in the reaction mixture. This carbonyl hydride species can be produced in the absence of H_2 by migration of H from the support to Rh. The dissociation of CO_2 on supported Rh has been shown to be enhanced by the presence of H_2 and impurity boron.

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I. Introduction

Although there has been a tremendous amount of research interest in recent years in catalytic methanation, most of this interest has been focused upon the hydrogenation of CO over various noble metal catalysts. The hydrogenation of CO_2 over these catalysts is at least of equal importance as a reaction relevant to international energy needs; however, there have been considerably fewer detailed studies of this reaction. Such recent studies have included CO_2 hydrogenation over Ni(100)[1], supported Ni[2-7], supported Pd[8,9], supported Pt and Ir[8], supported Ru[7,8,10-13], polycrystalline Rh[14,15], and supported Rh[8,10,16-22]. From prior work on CO_2 hydrogenation several generalizations can be made concerning the reaction.[1-22]

(1) CO_2 hydrogenation is much more selective toward product formation than is CO hydrogenation, with CH_4 generally being the only hydrocarbon product for the former.

(2) The activation energy for CO_2 hydrogenation is generally lower than that for CO hydrogenation under analogous conditions.

(3) The apparent rate of CH_4 formation from CO_2 hydrogenation is generally higher than that from CO hydrogenation under analogous conditions, with CH_4 generally being formed at lower temperatures for the CO_2 reaction.

(4) CO_2 hydrogenation is effectively poisoned by the presence of small amounts of gas-phase CO.

(5) CO_2 hydrogenation is generally thought to proceed via dissociation to some form of adsorbed CO and then along the same reaction pathway as that of CO hydrogenation.

In this paper we shall report on recent infrared studies of the hydrogenation of CO_2 over supported Rh catalysts with emphases on a carbonyl hydride intermediate and the dissociation of CO_2 over the catalysts under varying reaction conditions.

II. Experimental

Supported Rh catalyst films were prepared by procedures used here previously for infrared studies of CO adsorbed on supported Rh[23-25] and the hydrogenation of CO over supported Rh.[26] Briefly, sufficient $RhCl_3 \cdot H_2O$ (Alfa products, Inc.) was dissolved in one part triply distilled water and added to nine parts spectroscopic-grade acetone containing support material to produce catalysts having final weight percentages of Rh of either 0.5 or 10%. The support materials used were alumina (Degussa Aluminum Oxide C, 100 m^2g^{-1}), titania (Degussa Titanium Oxide P25, 50 m^2g^{-1}), and silica (Cabot Cab-O-sil M-5, 200 m^2g^{-1}). The slurry mixture of $RhCl_3 \cdot 3H_2O$, support, water, and acetone was carefully sprayed using a specially designed atomizer onto a 25 mm CaF_2 infrared window held at a temperature of ca. 360 K. The solvents rapidly vaporized leaving thin films of $RhCl_3 \cdot 3H_2O$/support adhered tightly to the window typically at ca. 4 mg cm^{-2}. The window containing the catalyst was then mounted in a specially designed Pyrex infrared cell (Figure 1), and the cell was evacuated at 298 K over night. The sample was heated under vacuum (2×10^{-6} Torr using an ion pump) for 1 hr at 460 K and generally subjected to hydrogen reduction

cycles at 470 K. The reduction cycles consisted of exposure to successive doses of H_2 or D_2 at 70 Torr for 5, 5, 10, and 20 min, with each cycle being followed by evacuation to at least 10^{-5} Torr. The reduced samples were then heated at 460 K under vacuum for an additional 30 min and evacuated to a base pressure of 1×10^{-6} Torr.

For a typical kinetics experiment the infrared cell was dosed with 66 Torr of a 1:4 mixture of CO_2:H_2 and rapidly heated to a prescribed temperature. The cell temperature was monitored by means of the measured voltage across the heating coils; calibration under reaction conditions was checked frequently with a chromel-alumel thermocouple. The production of methane during the reaction and the formation of surface intermediates were followed by infrared spectroscopy. The spectrometer (Perkin-Elmer model 983 with Perkin-Elmer data station) was operated at a resolution of 4.5 cm^{-1} in the 2000 cm^{-1} region. The infrared beam was blocked from the sample except during a data scan to minimize the additional heating effect of the beam on the sample. The yield of CH_4 produced at any given time in the reaction was determined by means of a calibration curve based upon the integrated intensities of the 3014 and/or 1304 cm^{-1} infrared bands for methane as a function of partial pressure of CH_4. The calibration curve was developed for each sample by evacuation of the cell at the end of the experiment followed by the introduction of CH_4 at known pressures in the presence of the supported Rh catalyst (MKS Baratron capacitance manometer) and associated infrared scans; an example of such a curve is shown in Figure 2.

For experiments involving isotopic labeling, dissociation of CO_2, introduction of impurity boron, etc., the procedures differed slightly from

the kinetics experiments and will be discussed later in the text. All gases employed in these experiments (H_2, D_2, CO_2, and CH_4) were of the highest purity obtainable from Matheson; all except CO_2 were passed through liquid nitrogen traps before use.

III. Results

Typical infrared spectra corresponding to the hydrogenation of CO_2 over 10% Rh/X (X=TiO_2, Al_2O_3, SiO_2) and 0.5% Rh/X (X=TiO_2, Al_2O_3) are shown in Figures 3-7. The bands of greatest interest in all of the spectra are those in the 2020-2040 cm^{-1} region which must be assigned to some form of an adsorbed CO species in that they are not removed by evacuation of the cell and the sharp bands at 1304 and 3014 cm^{-1} removed by evacuation of the cell which represent the accumulation of gas-phase CH_4. The CO band generally occurred at lower frequency for Rh/Al_2O_3 and Rh/SiO_2 than for Rh/TiO_2. The broad band of low intensity in Fig. 3c is representative of a bridged carbonyl species.[23-27] The extensive band structure in the 1600 cm^{-1} region of spectra 3b,c corresponds to the presence of gas-phase H_2O, while the broader bands near 1600 cm^{-1} which occur at 298 K (spectrum 3a) are indicative of a hydrated support and possibly also to the presence of carbonates and bicarbonates on the support. The bands in the 1400-2000 cm^{-1} region of spectrum 5a for 10% Rh/SiO_2 are present also for a film containing only SiO_2. It should be noted that none of the support materials as films catalyzed the production of measurable amounts of CH_4 under the reaction conditions employed in the experiments unless Rh was present. Blank support samples gave only bands characteristic of hydration, carbonates, and bicarbonates; no bands attributable to adsorbed

CO species were ever present.

The infrared spectra of 0.5% Rh/TiO_2 and 0.5% Rh/Al_2O_3 (Figures 6 and 7) are somewhat different than those for their 10% analogs. The ambient temperature spectra (6a and 7a) show more band structure indicative of hydration, carbonates, and bicarbonates in the 1400-1700 cm^{-1} regions than do those in 3a, 4a, and 5a. Furthermore, upon heating the 0.5% Rh/Al_2O_3 catalyst, bands near 1375 and 1586 cm^{-1} characteristic of a formate species[10,17,18,21,22] grew in; these bands were not evident under similar conditions for the 10% catalysts or the blank supports. Also, for the 0.5% supported Rh catalysts the band in the 2020-2040 cm^{-1} region is broader and weaker than the corresponding band for the 10% catalysts.

From reproducible infrared spectra for the various supported catalyst films, turnover frequencies (molecules CH_4/Rh atom/sec) were determined at several temperatures in the range 423-503 K. Comparisons of these turnover frequencies at 483 K for six samples for the hydrogenation of CO[26] and CO_2 are shown in Table I. Table I also shows the CO stretching frequencies for the adsorbed CO species for the various catalyst films. Typical Arrhenius plots using the turnover frequencies for 0.5% Rh/TiO_2 and 0.5% Rh/Al_2O_3 are shown in Figure 8. We have only examined the Rh/SiO_2 films at 483 K, and thus can not report activation energies for Rh/SiO_2 at this time. Activation energies evaluated from Arrhenius plots for 0.5 and 10% Rh/TiO_2 and Rh/Al_2O_3 have been presented in Table II together with prior data reported by other laboratories.

In an effort to identify the species responsible for the infrared bands in the 2020-2040 cm^{-1} regions of the spectra several other experiments were performed. Figure 9 illustrates the effect of isotopic

substitution on this band. For two analogous experiments in which CO_2 was hydrogenated (9a) and deuterated (9b) over 10% Rh/TiO_2 the band near 2030 cm^{-1} shifts to lower frequency upon deuteration by 8 cm^{-1}. The corresponding shift for 10% Rh/SiO_2 was 5 cm^{-1}. For 10% Rh/Al_2O_3 bands of comparable intensity for hydrogenation and deuteration were not obtained in the experiments performed and thus the shift was not measured. In spectrum 9b the bands at 2258 and 2199 cm^{-1} can be assigned to vibrational modes for CD_4 and CH_3D, respectively.[28] Bands corresponding to CHD_3 and CH_2D_2 are masked by broad structure near 2269 and 2255 cm^{-1}. The small band at 2141 cm^{-1} in spectrum 9b occurs only for deuteration and disappears upon evacuation of the cell and is thus not due to a surface species, but we can not propose an assignment for this band at this time. It should be added that the $D_2 + CO_2$ reaction clearly proceeded more rapidly than the $H_2 + CO_2$ reaction over the supported Rh films at a given temperature.

Figure 10 shows the effects of adding H_2 gas and/or boric acid to 10% Rh/TiO_2 catalysts. In experiments 10a and 10b the catalysts were heated for long periods of time at 523 K under vacuum following reduction to remove as much hydrogen from the support as possible; the catalyst corresponding to 10b had been doped with 4.9% H_3BO_3 before treatment. For 10c and 10d standard catalyst preparation was used (except H_3BO_3 was added for 10c). Then CO_2 was introduced alone (10 a or 10b) or with an excess of H_2 (10c or 10d). All of the samples were heated at 503 K for 4 hr. From a comparison of the CO species bands near 2030 cm^{-1}, it is evident that H_2 causes an increase in its intensity for nonboron-doped samples (10a and 10d), but a decrease in its intensity for boron-doped samples (10b and 10c). It is also apparent that the impurity boron species cause(s) a

reduction in the intensity of the CH_4 band at 1304 cm^{-1}. The large bands in the 1200-1600 cm^{-1} regions of spectra 10b and 10c can be attributed to boron oxides[29,30] which may be located primarily on the support.

IV. Discussion

General

From Table I it is evident that the turnover frequencies for the catalyzed CO_2 hydrogenation reaction are significantly larger than those for CO hydrogenation at a given temperature (483 K) for a given catalyst film with the possible exception of the 10% Rh/SiO_2 film. The latter result is probably not significant in that CH_4 yields were lower and infrared background interference was greater for the SiO_2 samples. In any case these observations are in accord with those of most other laboratories which have compared the rates of the two reactions over supported catalysts. From Table I one further notes that the catalytic activity of supported Rh for the hydrogenation of CO_2 depends upon the nature of the support, the order being $TiO_2 > Al_2O_3 > SiO_2$; this observation is also in accord with that elsewhere.[17,21] The turnover frequencies measured in this work for the 0.5% supported Rh catalyst films are substantially higher than those for the analogous 10% Rh films. This observation can most probably be attributed to the fact that the Rh is more highly dispersed in the 0.5% Rh films. It has been postulated that for a 0.5% supported Rh catalyst film, the active sites are isolated Rh^+ ions; while for a 10% supported Rh catalyst film, the active sites are a mixture of isolated Rh^+ ions and Rh^o metal clusters.[23-27] In our calculation of turnover frequencies, we have assumed that all Rh atoms are potentially active sites. The turnover frequencies for the 10% Rh films thus are at best minimum values, and the

data shown for 0.5% supported Rh are probably more accurate.

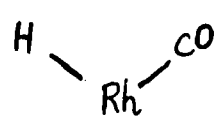
The data in Table II indicate that while turnover frequencies for Rh/TiO_2 are greater than those for Rh/Al_2O_3 at a given temperature, the reverse is true of the activation energies; the activation energy for hydrogenation of CO_2 over 0.5% Rh determined in this work was 24.5 kcal mol^{-1} for Rh/TiO_2, but only 15.6 kcal mol^{-1} for Rh/Al_2O_3. These results, both numerically and as a trend, are in reasonable agreement with prior results from other laboratories on a variety of Rh catalysts.[14,16,17] The trend was opposite for our 10% supported Rh catalyst films (21.4 and 20.3 kcal mol^{-1} for Rh/Al_2O_3 and Rh/TiO_2, respectively). Again this may reflect the error in the measurements of turnover frequencies due to varying active cluster sizes which may change with reaction temperature as discussed earlier for the 10% supported Rh catalysts. The significant support effect on the kinetics of the hydrogenation of CO_2 most likely are due to an electronic effect, in that TiO_2 is an n-type semiconductor, as pointed out by Solymosi and coworkers.[17] A partial reduction of the titania surface creating "special active sites" at the Rh-support interface may also be a factor.[31]

It is interesting that infrared bands characteristic of adsorbed formate were observed only for the 0.5% Rh/Al_2O_3 film following heating above 423 K. Solymosi and coworkers have detected formate in the CO_2 hydrogenation reaction and in the decomposition of formic acid over a variety of supported Rh catalysts even near 300 K; they have shown that the formate species resides on the support rather than on Rh, but that the presence of Rh is necessary for the formation of formate in the hydrogenation of CO_2.[10,17,18,22,32,33] It would appear from our data that

catalysts containing highly dispersed Rh on alumina (0.5% Rh/Al_2O_3) favor the formation of formate. Since formate does not form during the heating of Al_2O_3 alone in the presence of CO_2 and H_2, we would postulate that the Rh catalyzes the formation of formate, but in accord with the view of Solymosi, that the formate resides on the support well removed from the Rh-support interface.

The CO Intermediate

We performed isotopic labeling studies to insure that the infrared bands near 2030 cm^{-1} for these catalysts did not, in fact, correspond to a Rh-H vibrational mode. The band shifted to 1981 cm^{-1} when $C^{18}O_2$ was hydrogenated over 10% Rh/Al_2O_3 indicating that the band did not correspond to a Rh hydride. Figure 9 also clearly shows that this was not the case, because the band shift upon changing from H_2 to D_2 (typically in the range 5-10 cm^{-1} for all experiments) was indicative of isotopic substitution two bonds removed from the CO bond. Solymosi and coworkers have suggested that the 2030 cm^{-1} band is too low in frequency to correspond to a linear CO species, and most probably instead corresponds to a carbonyl hydride species.[17,18,22,34] Iizuka and coworkers, on the other hand, have pointed out that this band appears in the absence of gas-phase H_2 and have suggested that the band thus corresponds to the usual "linear" CO species at low coverage.[16,35] We concur completely with Solymosi. The band in the 2020-2040 cm^{-1} region is due to a carbonyl hydride species of the form shown below. The normal "linear" CO band frequency for supported Rh



catalysts lies in the range 2040 - 2080 cm^{-1} dependent upon coverage.[23-27] The hydride ligand acts as an electron donor through the metal into the antibonding * orbital on CO thus weakening the C-O bond and lowering its stretching frequency. The presence of two hydride ligands should enhance the effect and lower the stretching frequency further. The small isotopic shift observed here (5-10 cm^{-1}) upon switching from H_2 to D_2 gas is in accord with this explanation because the hydride (deuteride) ligand is two bonds removed from the CO oscillator. The two bands at 2036 and 2028 cm^{-1} in Figure 9 have the same intensity, so the low frequency of the CO moiety can not be due to low coverage; it must be due to the existence of the carbonyl hydride (deuteride). It should be noted that this band does move toward higher frequency as its intensity increases for the 10% Rh catalysts due to a coverage effect. However, it does not shift in frequency as coverage is increased for 0.5% Rh catalysts. This observation is in line with the 0.5% catalysts containing isolated Rh^+ ions, such that increasing coverage does not lead to increased dipole-dipole interaction causing shifts to higher frequency of the CO vibrational mode.[27] The existence of a carbonyl hydride band for CO_2 in the presence of supported Rh, but in the absence of gaseous H_2, has been observed here,[36] as well as by Iizuka and coworkers.[16,35] We believe that this is a result of migration of hydrogen from the support to the Rh, an "inverse spillover effect".[36] In support of this hypothesis, we have observed the presence of CHD_3 and CH_2D_2 over 10% Rh/TiO_2 at 503 K for a mixture of CO_2 and D_2 following reduction by D_2 and extensive heating in vacuum.[36] The H necessary for the formation of CHD_3 and CH_2D_2 must have come from the small amounts of unexchanged H on the support. We have also observed complete exchange of CH_4 in the presence of

D_2 over 10% Rh/TiO_2 at 503 K to form CH_3D, CH_2D_2, CHD_3, and CD_4.[36] All of these experiments demonstrate the mobility of H or D on the supported catalysts.

It should be noted also that our isotopic labeling studies have demonstrated an inverse isotope effect for the hydrogenation of CO_2 over all of the supported Rh films, ie. the turnover frequencies at a given temperature were larger for the production of CD_4 from $CO_2 + D_2$ than for the production of CH_4 from $CO_2 + H_2$. This inverse isotope effect has been noted by other laboratories for a variety of supported metal catalysts for CO and CO_2 hydrogenation.[16,37] Wilson [38] and Kellner and Bell[37] have concluded that the overall inverse isotope effect results from a combination of the kinetic and equilibrium isotope effects associated with the various steps of the mechanism.

The data in Table I concerning the carbonyl hydride band frequency for CO and CO_2 hydrogenation are suggestive of a monohydride in all cases for Rh/TiO_2, but possibly a dihydride for CO_2 hydrogenation over Rh/Al_2O_3 and Rh/SiO_2. The role of the carbonyl hydride species in the CO hydrogenation reaction was discussed in more detail elsewhere.[26]

The Dissociation of CO_2

Currently there exists a controversy concerning the dissociation of CO_2 over Rh at ambient temperature.[39-43] Somorjai and coworkers have reported that CO_2 does dissociate on Rh foil and on several different Rh single crystal surfaces with high probability (10^{-1}) at 300 K.[39] However, Weinberg has computed the probability of dissociative adsorption of CO_2 on Rh to be only 10^{-15} at low pressure and ambient temperature.[40] Goodman and

coworkers[41] have recently measured the activatiion energy for CO_2 dissociation on Rh(111) to be 17 kcal mol^{-1} and have concluded that the probability of dissociation of CO_2 on Rh at 300 K and 760 Torr is only 10^{-11}. Very recently Solymosi and Kiss have reported that no dissociation of CO_2 takes place on clean Rh at 300 K, but that dissociation does occur in the presence of H_2 or impurity boron.[42]

From spectrum 10a it is obvious that CO_2 dissociation does occur on 10% Rh/TiO_2 at 503 K in the absence of H_2 gas, for the carbonyl hydride infrared band at 2032 cm^{-1} grew to the indicated intensity after 4 hr. The necessary hydrogen for this species migrates to Rh from the support. We have made a similar observation for Rh/Al_2O_3. Examination of spectrum 10d reveals that the carbonyl hydride band was much more intense under the same conditions when gas-phase H_2 was present. We have shown previously that the carbonyl hydride band grows in intensity with time, even at 300 K, for 10% Rh/TiO_2 when H_2 gas is present.[43] Thus there can be no doubt that H_2 assists the dissociation of CO_2 on supported Rh. This is probably accomplished by a combination of two effects - reaction with adsorbed O produced from CO_2 decomposition to free active sites and more facile formation of the carbonyl hydride species.

Spectra 10b and 10c correspond to analogous experiments for 10% Rh/TiO_2 in which H_3BO_3 was added as in impurity. Comparison of spectra 10b and 10a shows that the presence of the impurity boron species (probably in the form of oxides) caused an accentuation of the carbonyl hydride species when no H_2 was present. This is most probably the result of electropositive boron interacting with the O in CO_2 to enhance dissociation and thus more facile formation of the carbonyl hydride species. On the

other hand, a comparison of spectra 10b and 10c reveals that the carbonyl hydride species is suppressed when impurity boron and gas-phase H_2 are present. Also from spectra 10c and 10d it is evident that impurity boron poisons the production of CH_4. These observations indicate that the impurity boron is poisoning the rate-determining step, probably by blocking active methanation sites. A build-up of carbon on inactive methanation sites due to the presence of H_2 in the reaction cell could then block the formation of additional carbonyl hydride and explain the weak infrared band for the latter.

Unfortunately we can not compute the probability of dissociation of CO_2 over Rh from our data. However, we suspect that the presence of impurities such as H_2, H from a support, or boron are necessary to make this process facile at low temperature.

Mechanism of CO_2 Hydrogenation

Based upon the data accumulated in these laboratories, we would propose that the mechanism of CO_2 hydrogenation over supported Rh catalyst films involves: (1) the dissociation of CO_2 on Rh assisted by the presence of H_2 gas or H from the support to form the Rh carbonyl hydride species, formate on the support, and adsorbed O on Rh; (2) the removal of adsorbed O by H_2 and H to form $H_2O_{(g)}$ and OH on the support; (3) dissociation of the C-O bond in the Rh carbonyl hydride, to form active C on Rh; and (4) reaction of the active surface C on Rh with H_2 and H(a) to form CH_4 (g). This proposed mechanistic scheme is very similar to one suggested earlier by Solymosi and coworkers.[22] Its most novel feature is the proposed carbonyl hydride intermediate.

The reason for CO_2 hydrogenation proceeding at an apparent faster rate than does CO hydrogenation, even though the mechanisms are thought to be similar, is that the reactions are negative order in CO; there is a lower steady-state concentration of CO for the CO_2 methanation process.[1] We agree with Goodman and coworkers that for CO_2 and CO methanation, there must be a delicate balance of the C(a) formation step and the C(a) surface hydrogen step,[1] such that either the dissociation of the carbonyl hydride or the hydrogenation of active C may be rate limiting, dependent upon reaction conditions. As for which step was rate determining for our catalyst films, we can only propose that for the impurity boron work, the rate determining step was hydrogenation of active C (see last section).

Conclusions

The following conclusions can be made from this work:

(1) Methane was the only hydrocarbon reaction product observed in these studies.

(2) There is a support effect for CO_2 hydrogenation over supported Rh catalyst films. The turnover frequencies at a given temperature are in the order $TiO_2 > Al_2O_3 > SiO_2$.
The CO_2 hydrogenation turnover frequencies are larger than CO hydrogenation ones under similar reaction conditions.

(3) The activation energy for hydrogenation of CO_2 is higher for Rh/TiO_2 than for Rh/Al_2O_3 for sample films containing low weight percent Rh.

(4) A formate species is formed upon heating for catalyst films

containing low Rh loading on Al_2O_3 indicating the possibility of location on the support well removed from the Rh-support interface. The formate species was not observed for catalyst films containing high Rh loading or on blank supports.

(5) A Rh carbonyl hydride species is formed during CO_2 hydrogenation which is a key observable intermediate in catalytic methanation. This intermediate has been observed for CO hydrogenation over supported Rh films also.[26] The carbonyl hydride can be formed as a result of hydrogen migration from the support in the absence of gas-phase H_2.

(6) The presence of H_2, H(a), and impurity boron all enhance the dissociation of CO_2 over supported Rh. However, impurity boron poisons the methanation reaction.

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TABLE I: Comparison of Turnover Frequencies for Hydrogenation of CO[a] and CO_2 over Supported Rh Catalyst Films at 483 K

Catalyst Film	$CO + 3H_2$ Rh(CO)H	$CO + 3H_2$ TN[b]	$CO_2 + 4H_2$ Rh(CO)H	$CO_2 + 4H_2$ TN[b]
10.0% Rh/TiO_2	2045[c]	19.1	2042[c]	81.3
10.0% Rh/Al_2O_3	2045	11.2	2025	33.5
10.0% Rh/SiO_2	2045	13.8	2028	9.2
0.5% Rh/TiO_2	2043	27.5	2038	803.0
0.5% Rh/Al_2O_3	2045	7.3	2020	77.8
0.5% Rh/SiO_2	2040	5.3	2032	30.4

[a]Reference 26.
[b]Molecules CH_4/Rh atom/sec x 10^5.
[c]Frequency in cm^{-1}.

TABLE II. Comparison of Activation Energies for Hydrogenation of CO_2 over Supported Rh Catalyst Films from This Work with Selected Values from Other Laboratories

Catalyst	Reaction Conditions	E_a[a]	Reference
0.5% Rh/Al_2O_3	66 Torr, 1:4	15.6	This work
0.5% Rh/TiO_2	CO_2: H_2,	24.5	This work
10.0% Rh/Al_2O_3	Static	21.4	This work
10.0% Rh/TiO_2		20.3	This work
Rh Foil	700 Torr, 1:3 CO_2: H_2, Flow	16	14
5% Rh/Al_2O_3	760 Torr, 1:4	16.2	17
1% Rh/TiO_2	CO_2:H_2, Flow	19.4	17
2.3% Rh/Al_2O_3	75 Torr, 1:4 CO_2:H_2, Flow	17.0	16

[a]Kcal mol^{-1}.

Figure Captions

Figure 1. Schematic of the Pyrex infrared cell/reactor used in this work.

Figure 2. Typical calibration curve for determining the reaction yield of methane.

Figure 3. Infrared spectra of a 10% Rh/TiO_2 film (4.7 mg cm^{-2}) following normal sample pretreatment and reduction and then: (a) introduction of 66.2 Torr CO_2 + $4H_2$ at 298 K, (b) heating at 503 K for 30 min, (c) heating at 503 K for 4 hr.

Figure 4. Infrared spectra of a 10% Rh/Al_2O_3 film (3.1 mg cm^{-2}) following normal sample pretreatment and reduction and then: (a) introduction of 66.4 Torr CO_2 + $4H_2$ at 298 K, (b) heating at 503 K for 1.5 hr, (c) heating at 503 K for 5 hr.

Figure 5. Infrared spectra of a 10% Rh/SiO_2 film (5.1 mg cm^{-2}) following normal sample pretreatment and reduction and then: (a) introduction of 66.1 Torr CO_2 + $4H_2$ at 298 K, (b) heating at 483 K for 1 hr, (c) 3 hr, (d) 8 hr.

Figure 6. Infrared spectra of a 0.5% Rh/TiO_2 film (4.4 mg cm^{-2}) following normal sample pretreatment and reduction and then: (a) introduction of 66.5 Torr CO_2 + $4H_2$ at 298 K, (b) heating at 443 K for 2 hr, (c) heating at 443 K for 7 hr, (d) evacuation at 298 K.

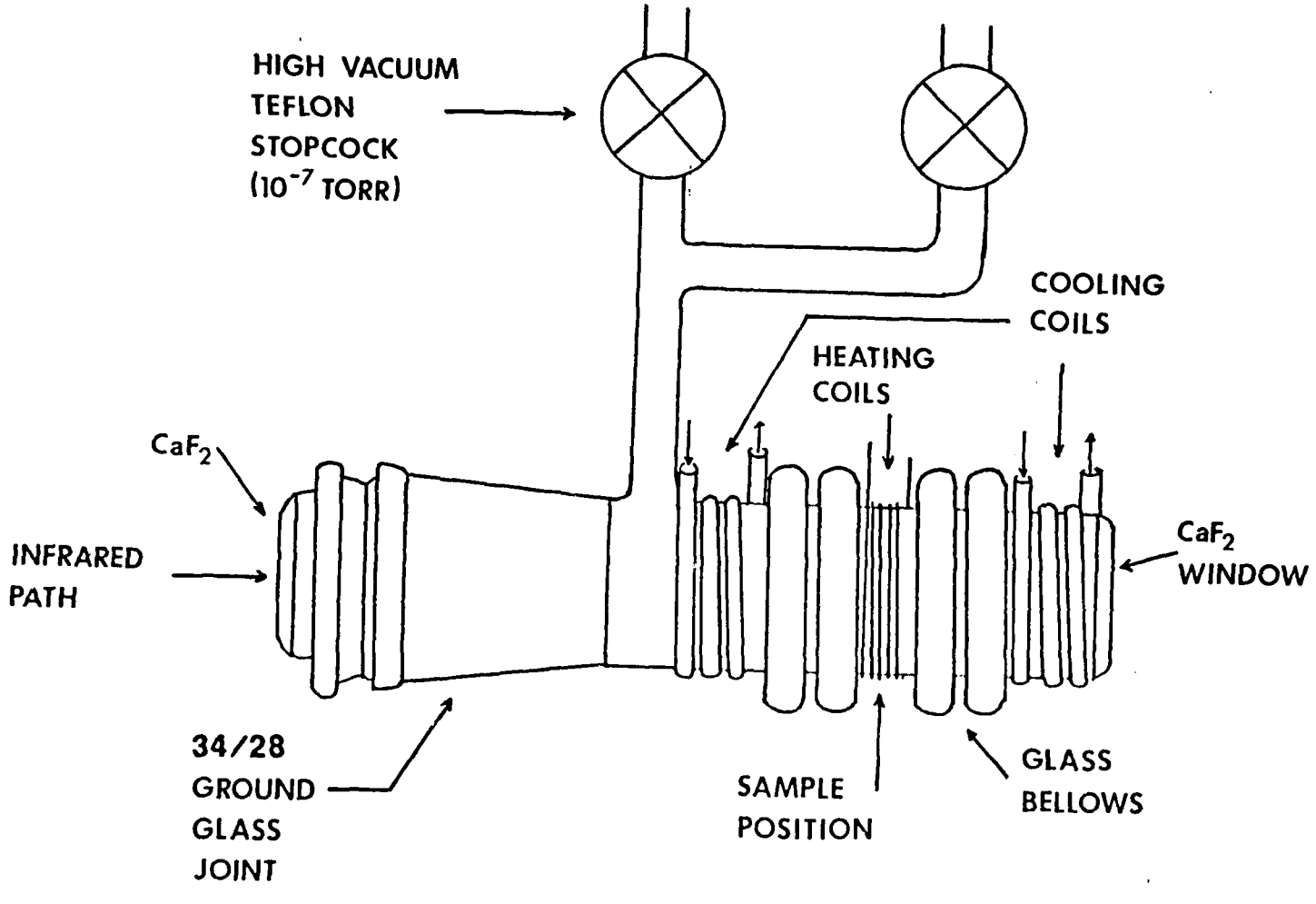
Figure 7. Infrared spectra of a 0.5% Rh/Al_2O_3 film (4.4 mg cm^{-2}) following normal sample pretreatment and reduction and then:

(a) introduction of 66.3 Torr CO_2 + $4H_2$ at 298 K, (b) heating at 453 K for 2 hr, (c) heating at 453 K for 3 hr, (d) heating at 453 K for 16 hr, (e) evacuation at 298 K.

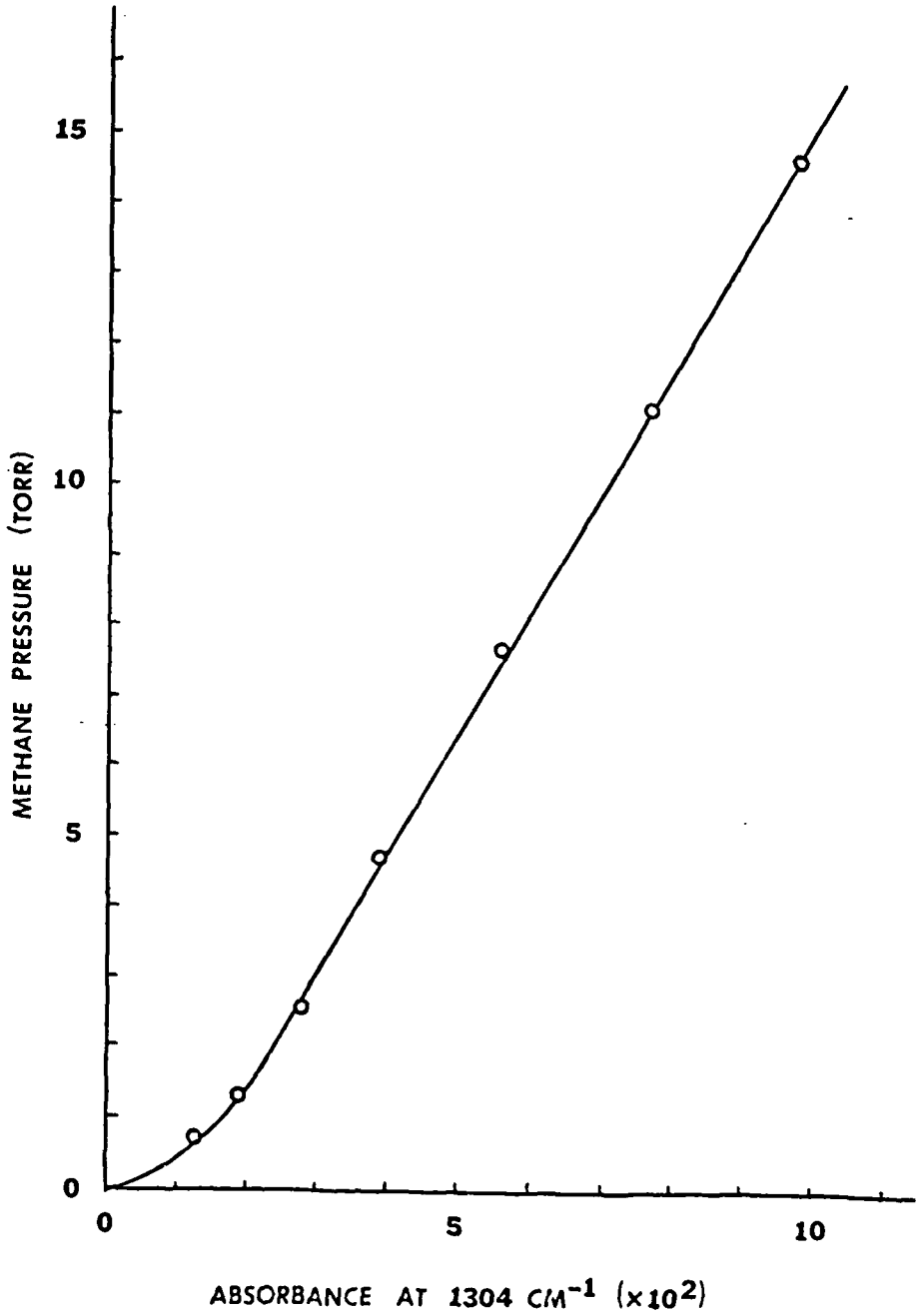
Figure 8. Typical Arrhenius plots for CH_4 production from 66 Torr CO_2 + $4H_2$ over 0.5% Rh/TiO_2 and 0.5% Rh/Al_2O_3 films. Activation energies in kcal mol^{-1} are indicated.

Figure 9. Infrared spectra of 10% Rh/TiO_2 films: (a) 4.7 mg cm^{-2} film following normal pretreatment, reduction in H_2, introduction of 66.2 Torr CO_2 + $4H_2$, and heating at 503 K for 2 hr, (b) 4.2 mg cm^{-2} film following normal pretreatment, reduction in D_2, introduction of 66.0 Torr CO_2 + $4D_2$, and heating at 503 K for 2 hr.

Figure 10. Infrared spectra of 10% Rh/TiO_2 films: (a) 4.1 mg cm^{-2} film following reduction, heating at 523 K at $1x10^{-6}$ Torr for 16 hr, introduction of 12.6 Torr CO_2, and heating at 503 K for 4 hr, (b) 4.4 mg cm^{-2} film doped with 4.9% H_3BO_3, following reduction, heating at 523 K at $1x10^{-6}$ Torr for 17.7 hr, introduction of 12.9 Torr CO_2, and heating at 503 K for 4 hr, (c) 4.2 mg cm^{-2} film doped with 4.9% H_3BO_3, following standard reduction, introduction of 66.2 Torr CO_2 + $4H_2$, heating at 503 K for 4 hr, (d) 4.3 mg cm^{-2} film following standard reduction, introduction of 66.2 Torr CO_2 + $4H_2$, heating at 503 K for 4 hr.



Worley et al. Fig. 1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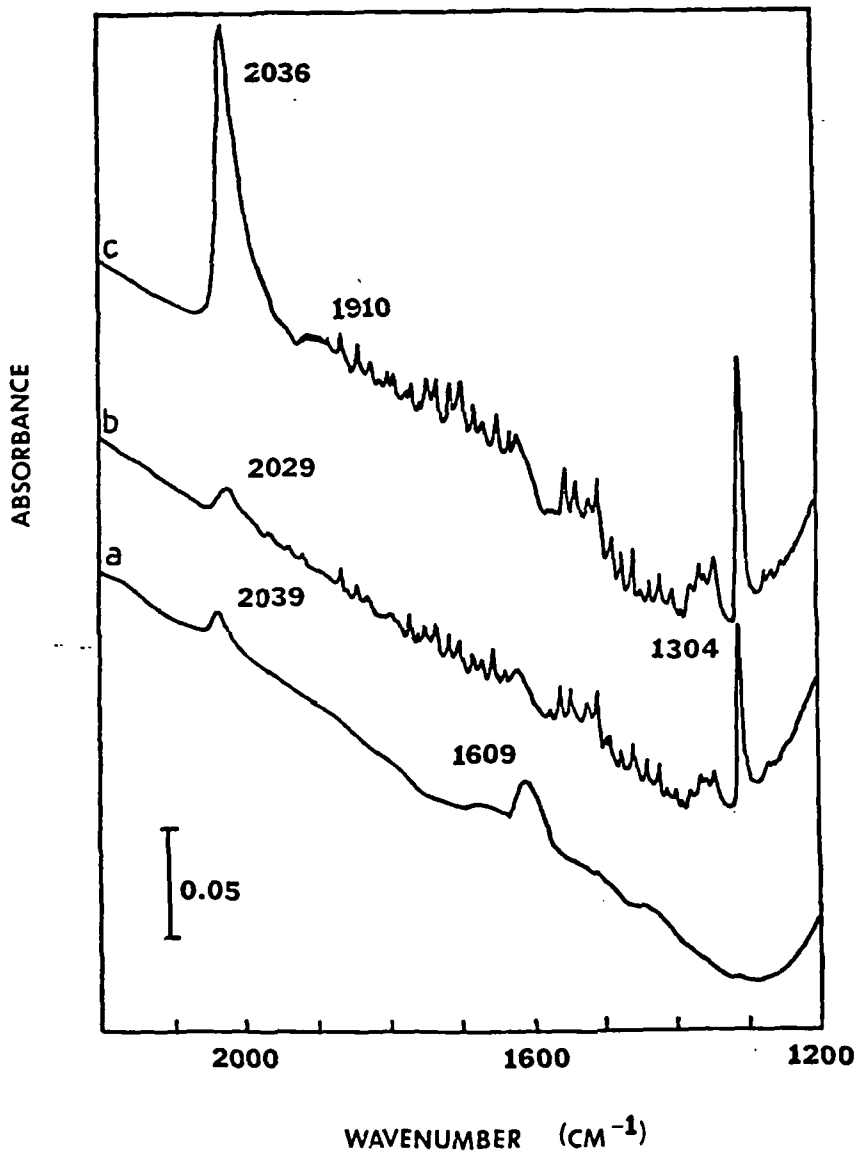
10
5
0
0
5
10
ABSORBANCE AT 1304 CM^{-1} ($\times 10^2$)

2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1910
b
2029
a
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2000
1600
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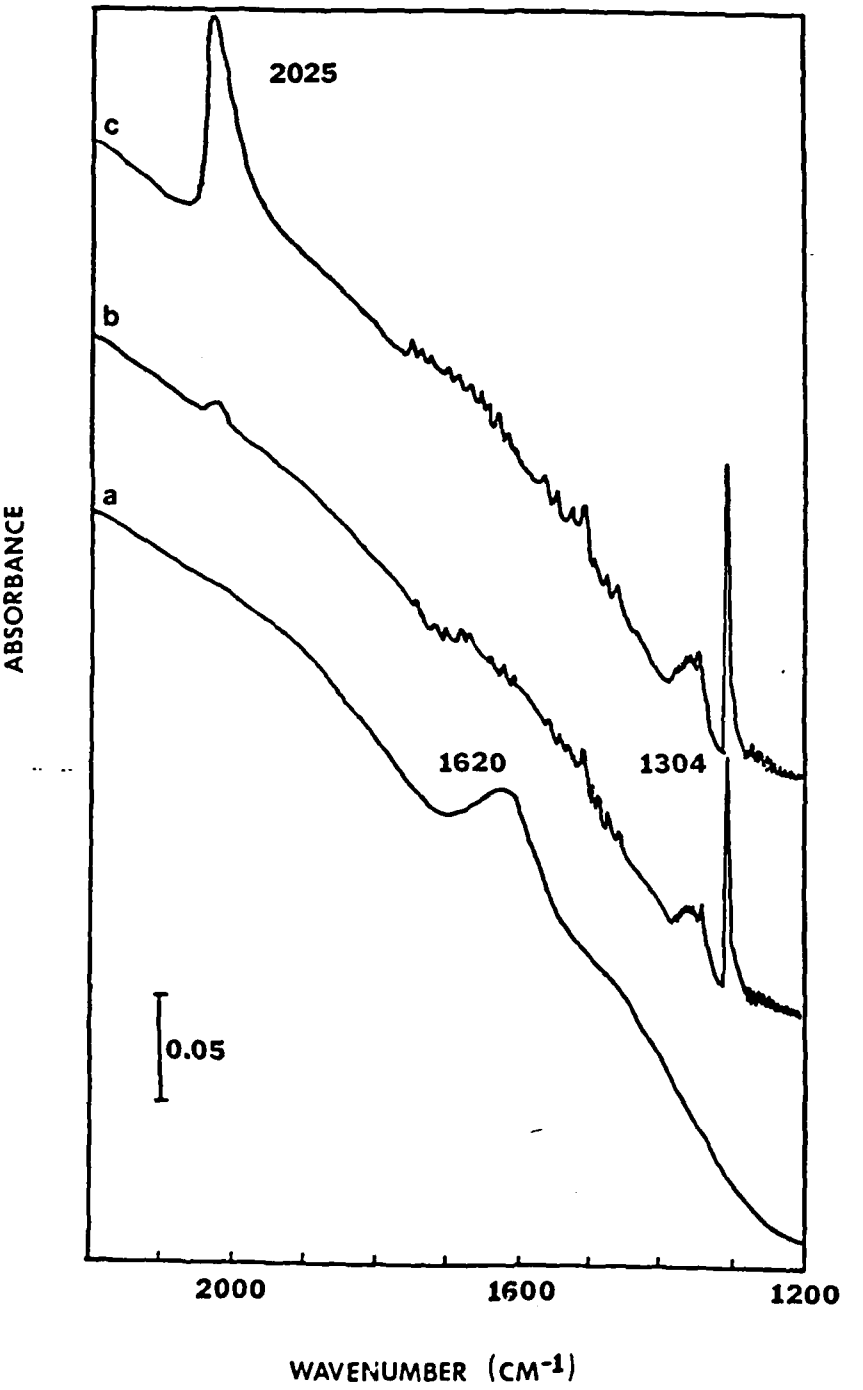
WAVENUMBER (CM^{-1})



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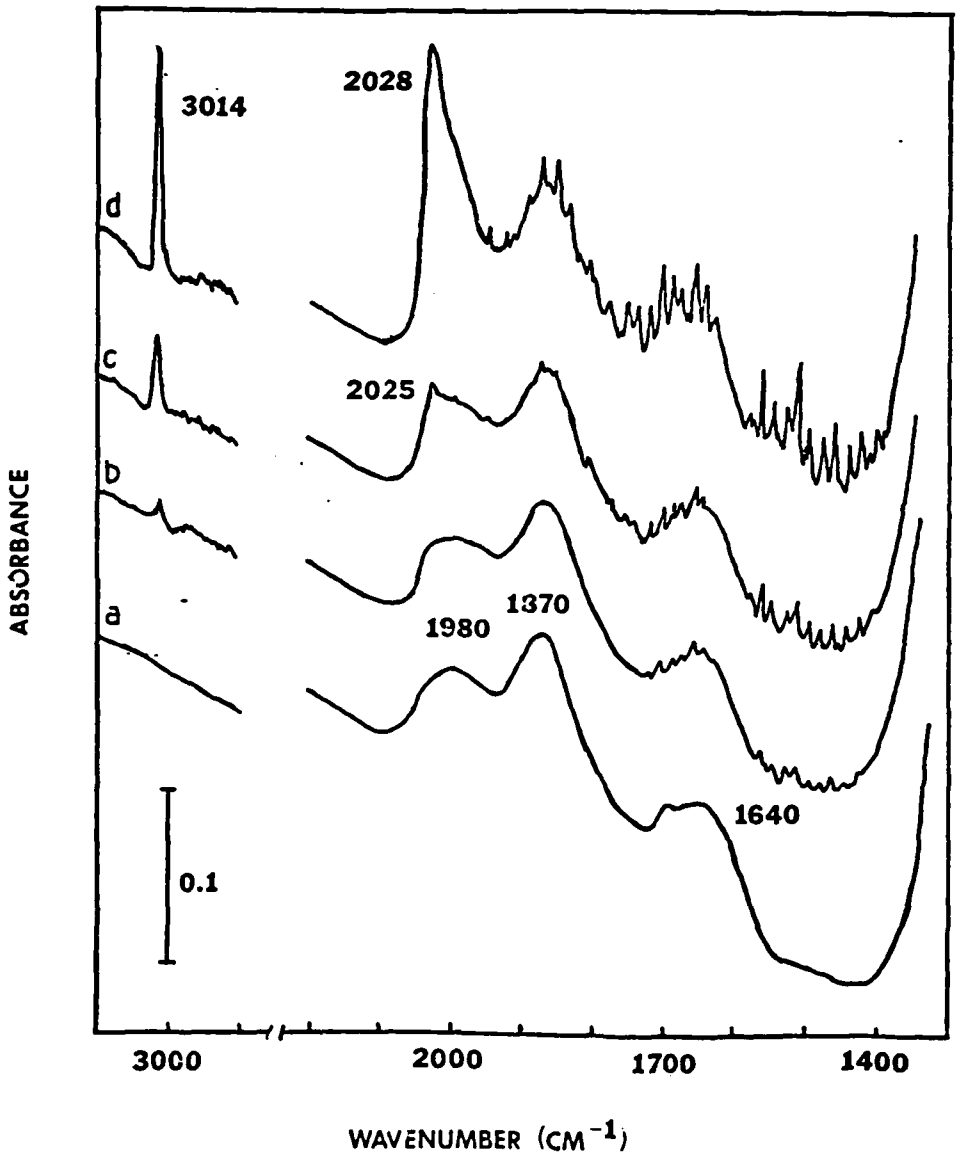
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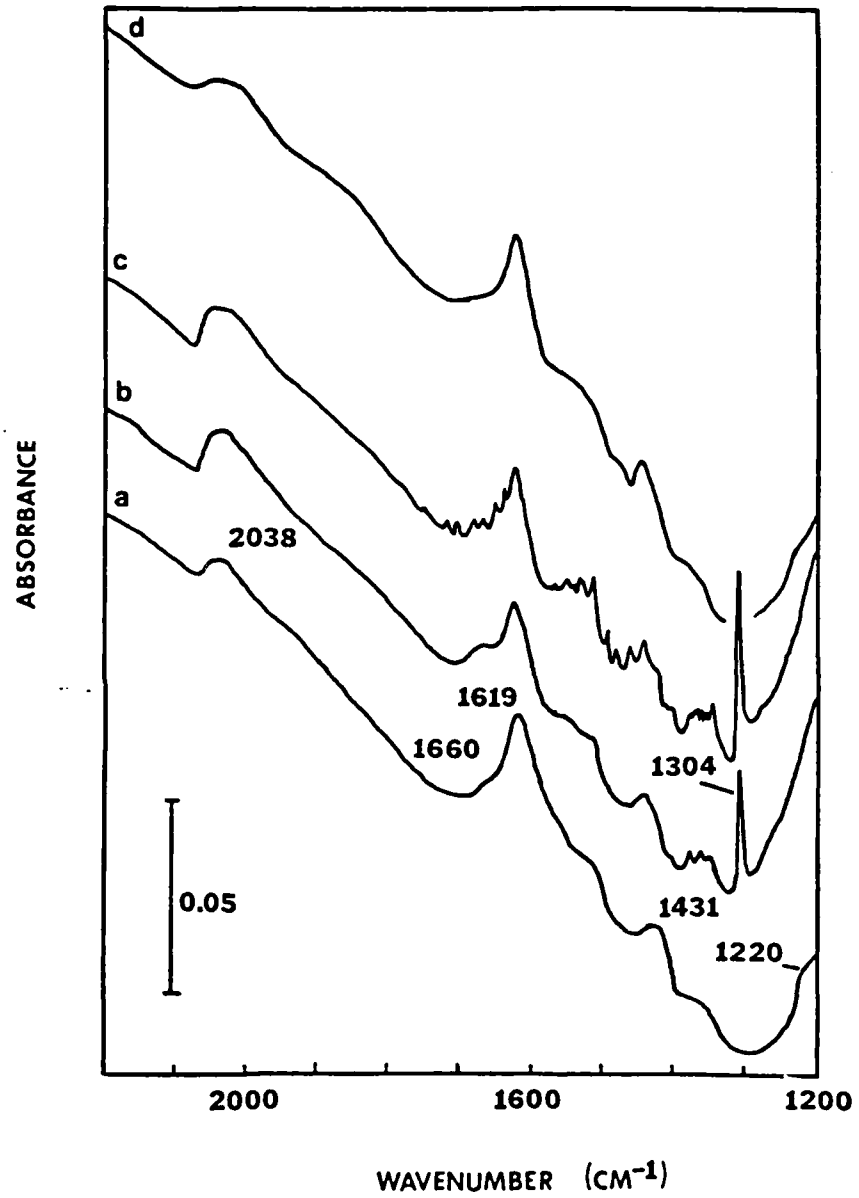
1400
WAVENUMBER (CM^{-1})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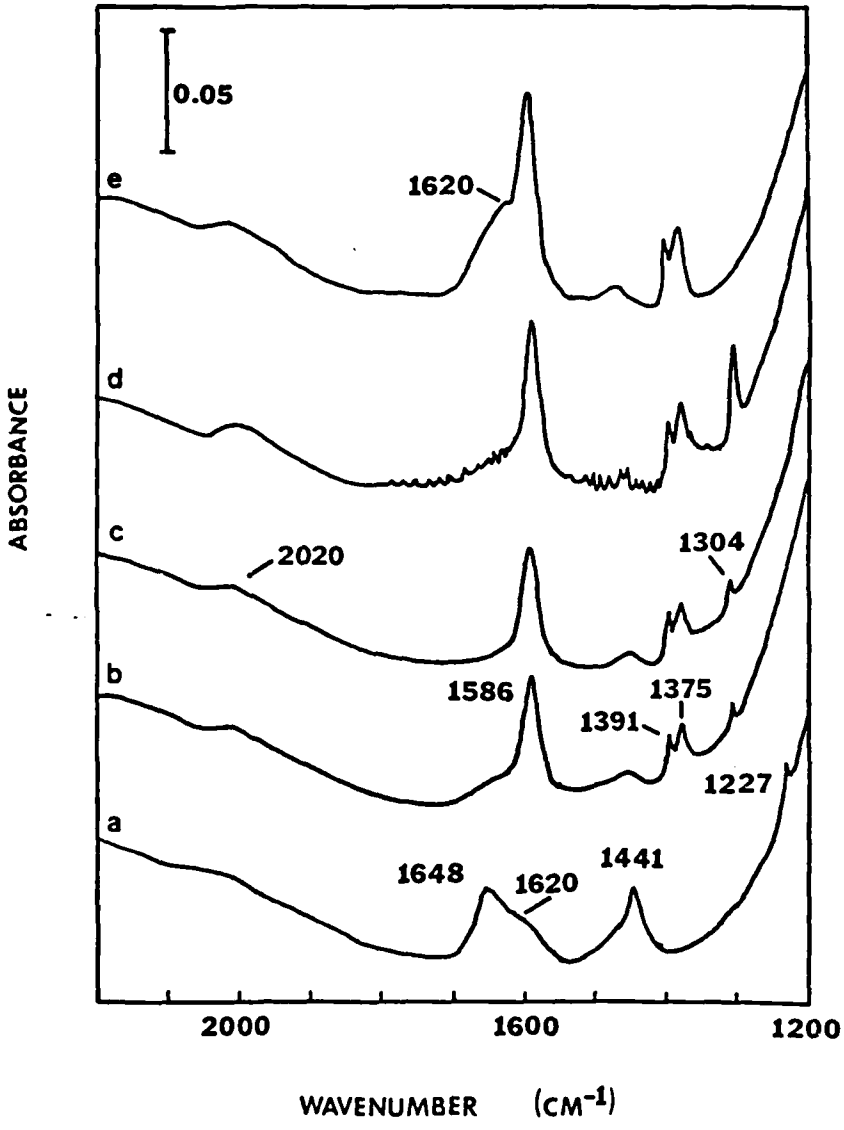
WAVENUMBER (CM^{-1})

Yorkey etc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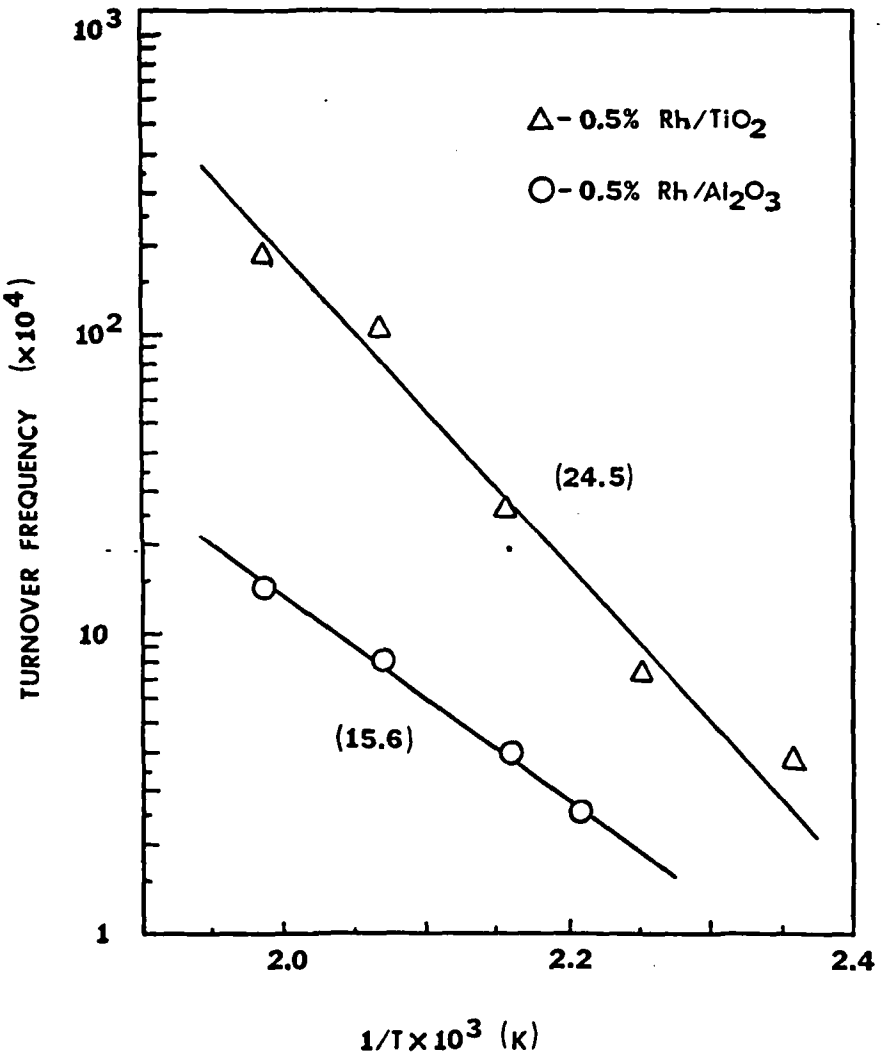
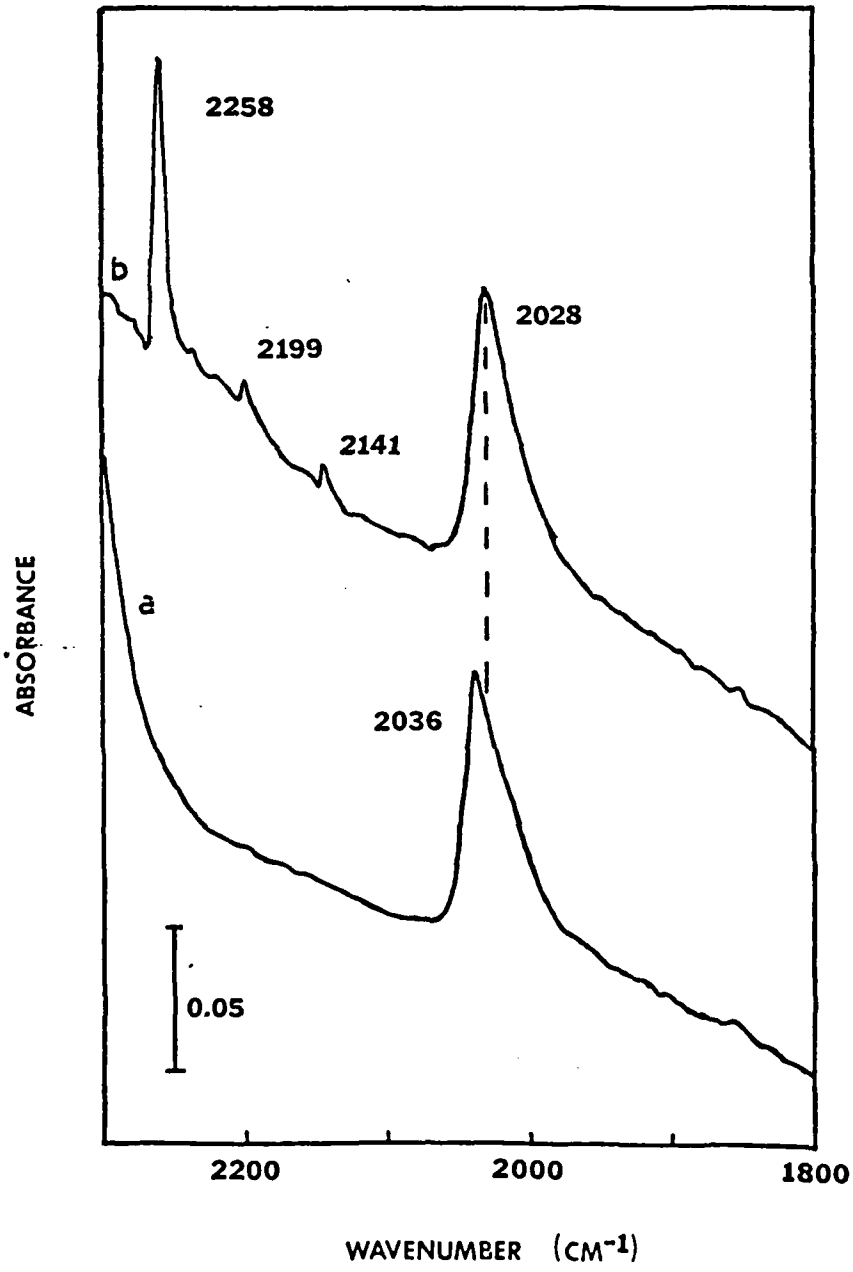
2000
1600
1200
WAVENUMBER (CM-1)

Wesley, et al.


10^3
10^2
10
1
TURNOVER FREQUENCY ($\times 10^4$)
Δ - 0.5% Rh/TiO_2
O - 0.5% Rh/Al_2O_3
(24.5)
(15.6)
2.0
2.2
2.4
$1/T \times 10^3$ (K)

Wong, et al.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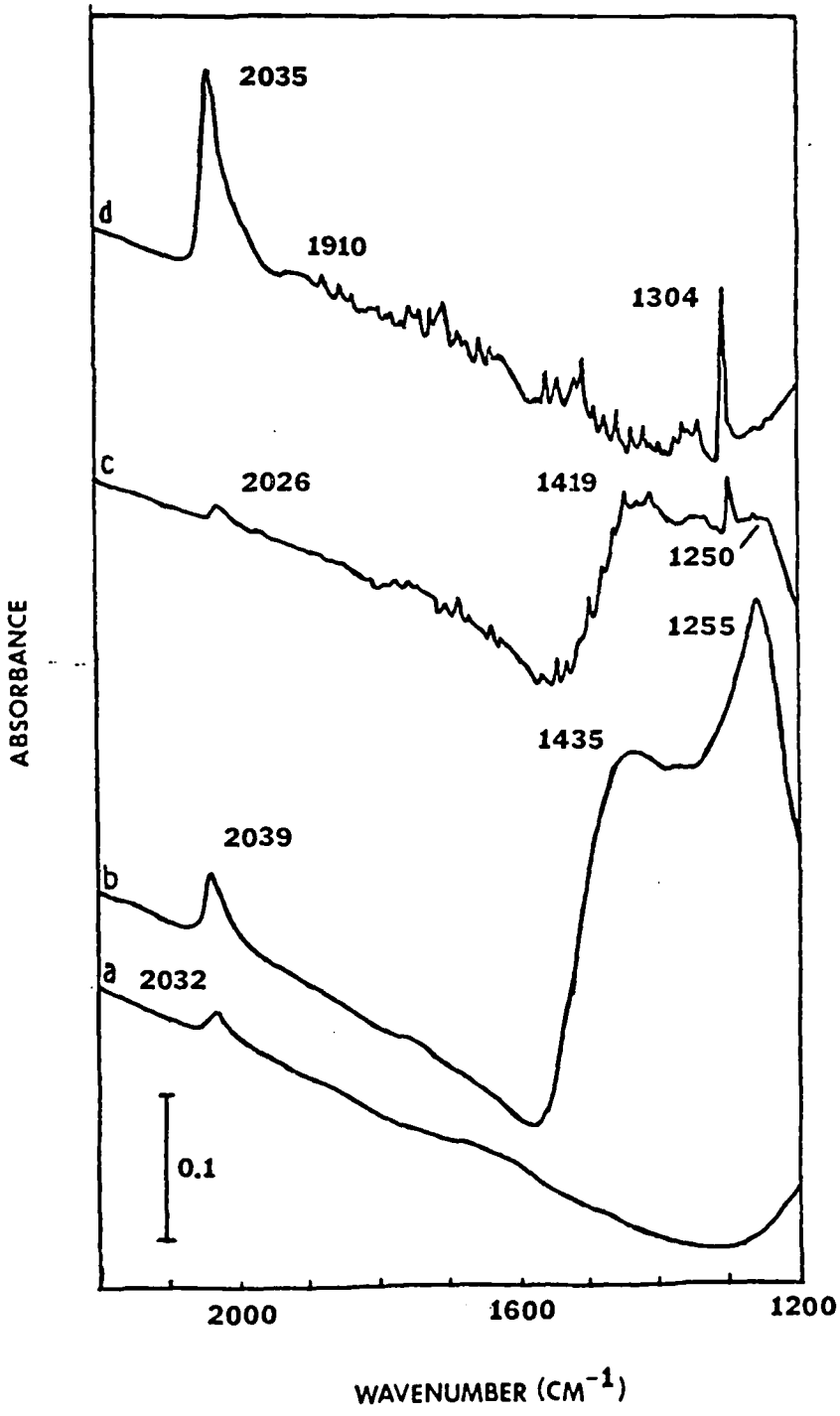
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0.1
2000
1600
1200
WAVENUMBER (CM^{-1})

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