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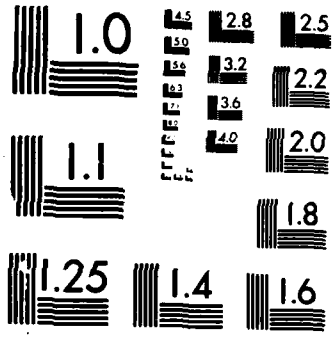

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THE EFFECTS OF POTASSIUM ON CARBON MONOXIDE METHANATION OVER SUPPORTED RHODIUM FILMS

BY

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The Effects of Potassium on Carbon Monoxide Methanation over Supported Rhodium Films

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Abstract

The reaction of hydrogen with carbon monoxide over Rh/Al_2O_3 and Rh/TiO_2 catalytic films, some of which contained potassium as an additive, has been investigated. The presence of potassium caused the usual gem dicarbonyl and linear CO species on supported rhodium to dissociate at lower temperature than for catalysts containing no potassium. On the other hand, the bridged carbonyl species was significantly enhanced by the presence of potassium. The Rh/TiO_2 films to which potassium was added catalyzed the production of significant amounts of acetone and acetaldehyde as oxygenated products. It is likely that the bridged carbonyl species is the precursor to oxygenated products.

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Introduction

There has been considerable interest in the effects of alklai metal promotors in catalytic reactions.[1] Solymosi and coworkers have suggested that the additives electronically affect metal-support interaction and thus influence catalytic activity.[2] Although generally hydrogenation of carbon monoxide and especially carbon dioxide over supported rhodium catalysts produces methane as the primary product,[3] the selectivity at least for CO hydrogenation can be altered toward enhanced yields of oxygenated products by using alkali promotors.[4] Goodwin and coworkers have shown recently that added potassium causes the selectivity for CO hydrogenation of a 3% Rh/TiO_2 catalyst to shift toward oxygenated products with acetaldehyde and acetone being present in significant quantities.[5] It is the purpose of this letter to report preliminary data from these laboratories concerning the hydrogenation of CO over Rh/Al_2O_3 and Rh/TiO_2 catalytic films containing potassium as an additive.

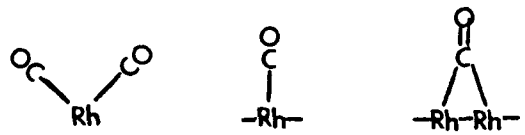
Experimental Section

The Rh/Al_2O_3 and Rh/TiO_2 catalysts used in this study were prepared in a manner similar to those studied previously here.[3,6] Briefly, acetone/water solutions containing appropriate amounts of $RhCl_3 \cdot 3H_2O$, KCl, and alumina (Degussa Aluminum Oxide C, 100 m^2g^{-1}) were carefully sprayed using a specially designed atomizer onto a heated 20 mm CaF_2 infrared window. Evaporation of the solvents left a uniform thin film (typically 4.3 mg cm^{-2}) of the mixed solid materials adhered to the window. The window containing the film was mounted inside an infrared cell reactor[3] which was evacuated overnight. The sample film was then evacuated at 470 K for 1 h, reduced at 480 K by 85 Torr doses of hydrogen for 5, 5, 10, and 20 min periods (each period followed by evacuation to ca. 10^{-5} Torr), and then

evacuated for an additional hour at 480 K to a base pressure of 10^{-6} Torr. For a typical experiment the cell was then exposed to a $CO:H_2$ mixture (1:4) at ca. 82.5 Torr total pressure and heated rapidly to some prescribed temperature. Methane gas and surface intermediate formations during the reaction were monitored by infrared spectroscopy (Perkin Elmer 983 with data system);[3] product distributions at the end of the experiment were measured by gas chromatography (Carle 400). Pressure measurements were made with an MKS Baratron capacitance manometer ($\pm$0.01 Torr).

Results and Discussion

The interaction of CO with supported Rh catalysts has been the subject of quite a few infrared studies.[7] Primarily three surface species have been generally identified as shown below. Species I, commonly referred to



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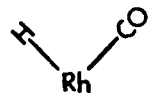
as the "gem dicarbonyl" species, exhibits two sharp infrared bands near 2030 and 2100 cm^{-1} which do not shift in wavenumber with coverage. This fact in conjunction with the fact that this is the only CO species observed for catalysts having very low Rh loading (eg. 0.5%) has led some workers to postulate that species I refers to Rh in a highly dispersed state, possibly even isolated Rh atoms. However, it is now apparent that the presence of CO itself may be necessary to cause the highly dispersed state of Rh necessary to produce species I.[8,9] Work in these laboratories[6] and elsewhere[10] has demonstrated that species I contains Rh in the +1 oxidation state. Species II, the "linear CO" species and species III, the "bridged carbonyl" species, exhibit infrared bands in the regions 2040-2080 cm^{-1} and

1840-1920 cm^{-1}, respectively; these bands do shift to higher frequency as CO coverage is increased and occur only for catalysts of higher Rh loading (>1%). Species II and III contain clusters of Rh atoms in the zero oxidation state. It has been of interest in these laboratories to observe changes in these surface species upon perturbation of the system. For example, it has been shown that when CO is hydrogenated at 483 K, species I and II are lost, and a carbonyl hydride species exhibiting an infrared band near 2040



cm^{-1} is formed which seems to be a precursor to the production of methane.[6d] Solymosi and coworkers first identified this species,[11] and we have proved its existence using isotopic labeling.[6f]

Figure 1 shows the result of reaction of H_2 and CO over a 2.2% Rh/Al_2O_3 catalyst film as a function of temperature. It is apparent that species I completely disappears between 390 and 430 K before the 1304 and 3015 cm^{-1} bands for methane gas are observed. At 480 K the identifiable surface species present during the production of methane are the carbonyl hydride species (2047 cm^{-1}) and bridged species III. Figure 2 shows the effects of potassium as an additive. Species I disappears at lower temperature, the carbonyl hydride species appears to be present in lower concentration, the concentration of species III appears to be greatly enhanced, and the methanation reaction is poisoned. Even at 300 K all infrared bands except the bridged carbonyl band are decreased in intensity. Also the species III band shifts to lower wavenumber as the temperature is increased even though it does not decline in intensity. We have observed

that for a 0.5% Rh/Al_2O_3 film, for which only species I is observed, that at a CO background pressure of 1×10^{-3} Torr with no hydrogen present the gem dicarbonyl infrared bands disappear between 430 and 460 K without potassium present, but between 380 and 430 K when potassium is present. Of course, without H_2 present no carbonyl hydride infrared band is observed in this case. The fact that species I is lost at lower temperature when potassium is present probably indicates that an electronic effect is operable causing an enhanced dissociation of CO in this species. On the other hand, the enhanced concentration of species III in the presence of potassium probably is due to a steric effect, ie. potassium blocks linear species II sites forcing CO to adopt multiple Rh sites, and hence leads to an increase in intensity of the species III infrared band. Insignificant amounts of oxygenated products were detected for H_2/CO over potassium-doped Rh/Al_2O_3 as expected; selectivity for oxygenated products in this reaction is favored by higher basicity in the support material than that exhibited by Al_2O_3.[4]

Figure 3 shows a comparison of CO hydrogenation over a 2.2% Rh/TiO_2 film with and without the presence of potassium. The results are similar to the Rh/Al_2O_3 experiments in that potassium causes a decline in intensity of all infrared bands except the broad species III band. Clearly the methanation reaction is poisoned, but oxygenated products are now observed. In spectrum 3d the bands at 1743, 1350, and 1220 cm^{-1} which disappear upon evacuation are due to acetone. Gas chromatographic analyses of the products produced in the infrared cell showed acetone (12.2%) and acetaldehyde (10.8%) as primary oxygenated products; both of these products were produced in higher yield when potassium was present (other products were methane 42.8%, ethane 8.6%, and carbon dioxide 25.7%). Goodwin and

coworkers[5] have also observed these products for CO hydrogenation over potassium-doped Rh/TiO_2, (K:Rh=1:2), although they found slightly more acetaldehyde (12.4%) than acetone (10.4%); their reaction conditions (1-10 atm, 523-708 K, $CO:H_2$ = 2:1) were quite different from those employed in this study, but the results of the two studies are very similar. It is generally believed that oxygenated products in the CO hydrogenation reaction result from reaction of undissociated CO with hydrocarbon fragments.[5] Since the presence of potassium enhances the formation of the bridged carbonyl species at the expense of the other CO species, it is probable that the bridged species is the precursor to the oxygenated products. The gem dicarbonyl and linear CO species most likely dissociate at low temperature to form carbon, and the carbonyl hydride species when hydrogen is present. At slightly higher temperature the active carbon is hydrogenated to methane and higher hydrocarbons. The hydride moiety also enhances the dissociation of the CO moiety in the carbonyl hydride species leading to further production of hydrocarbons.

The potassium probably functions in several roles. It enhances CO dissociation through an electronic effect which should lead to an increased production of methane and higher hydrocarbons unless inactive carbon is produced. It sterically blocks active methanation sites and causes the formation of an increased amount of bridged carbonyl species which is most probably the precursor to oxygenated products. Finally, there is increasing evidence that potassium may form cluster complexes with CO or exhibit short or long-range interactions with CO on transition metals;[12-17] this could also lead to ultimate dissociation to inactive carbon and to steric blockage of active Rh sites. Further work is in progress regarding

CO and CO_2 hydrogenation kinetics over potassium-doped supported rhodium catalysts.

Acknowledgments

The authors gratefully acknowledge the support of the Office of Naval Research for this work.

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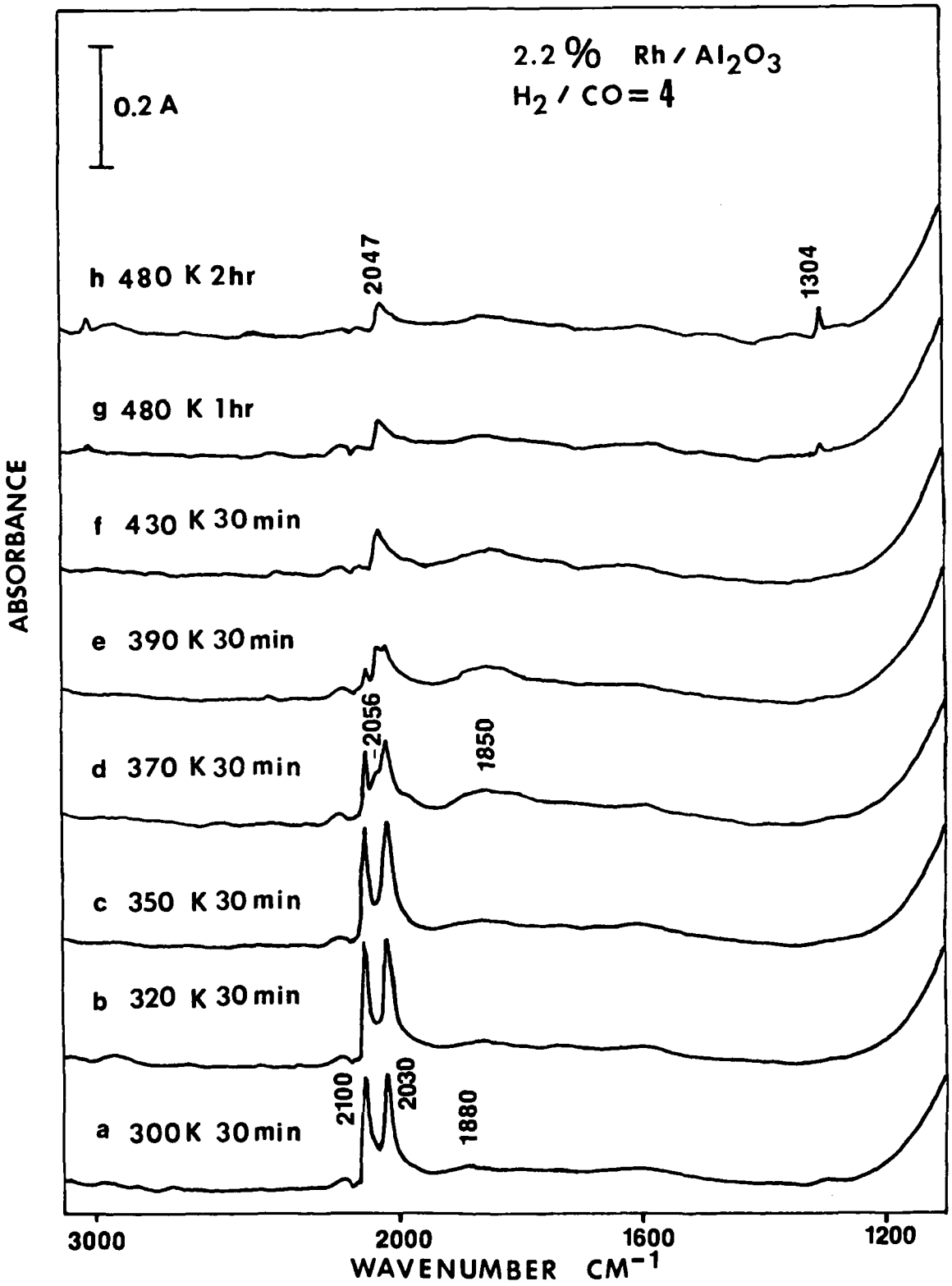
Figure Captions

Figure 1. Infrared spectra for the interaction of H_2 and CO over a 2.2% Rh/Al_2O_3 film (4.3 mg cm^{-2}) at a total pressure of 82.5 Torr as a function of temperature.

Figure 2. Infrared spectra for the interaction of H_2 and CO over a 2.2% Rh/Al_2O_3 film (4.3 mg cm^{-2}) to which potassium has been added at a total pressure of 82.5 Torr as a function of temperature.

Figure 3. Infrared spectra for the interaction of H_2 and CO over 2.2% Rh/TiO_2 films (4.3 mg cm^{-2}) with or without potassium added as indicated; total pressure was 82.5 Torr.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g 480 K 1hr
f 430 K 30 min
e 390 K 30 min
d 370 K 30 min
c 350 K 30 min
b 320 K 30 min
a 300K 30 min
2047
1304
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2100
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1880
ABSORBANCE
3000
2000
1600
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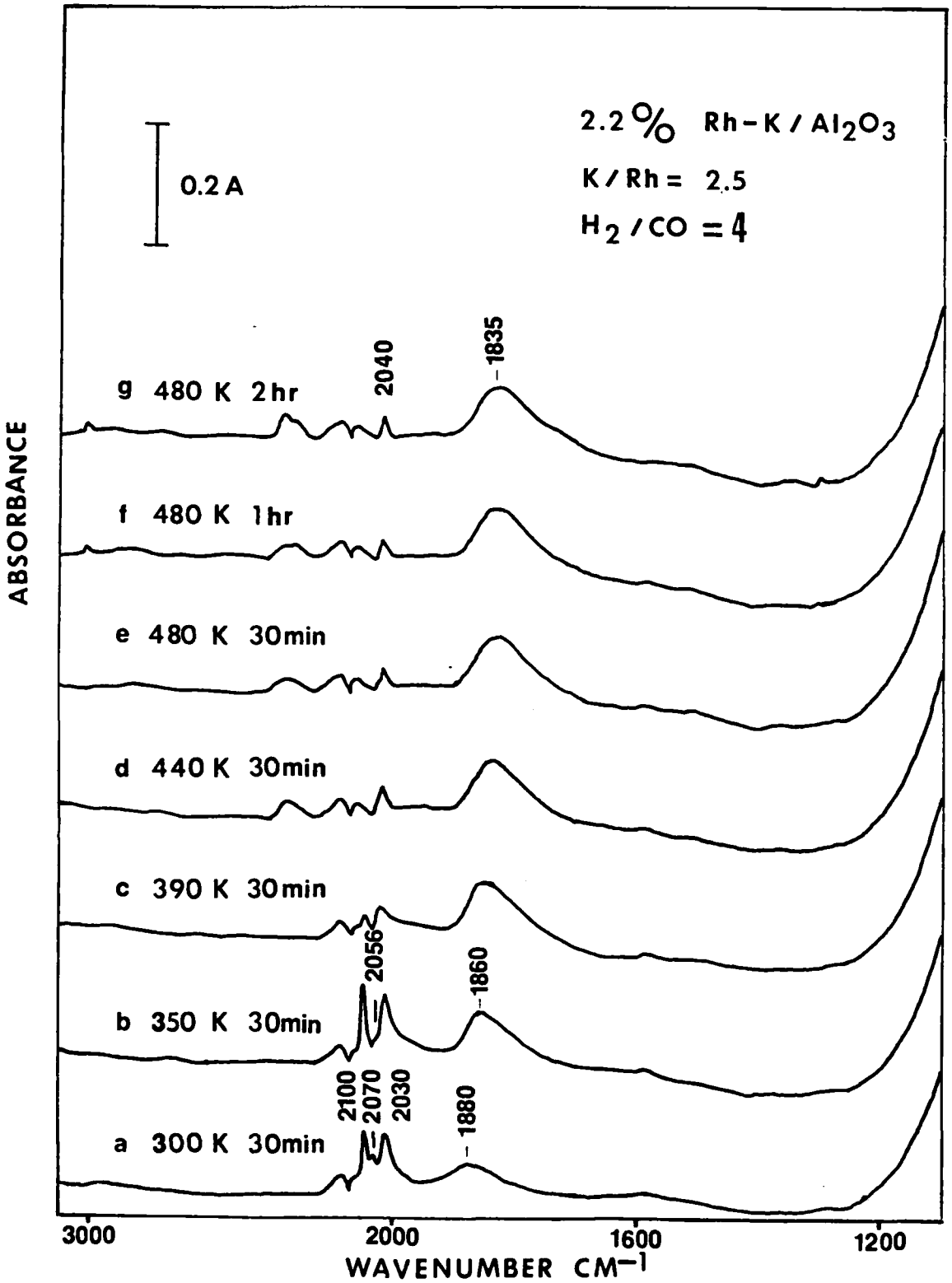
WAVENUMBER CM-1


2.2 % Rh-K / Al2O3
K / Rh = 2.5
H2 / CO = 4
0.2 A
g 480 K 2hr
f 480 K 1hr
e 480 K 30min
d 440 K 30min
c 390 K 30min
b 350 K 30min
a 300 K 30min
2040
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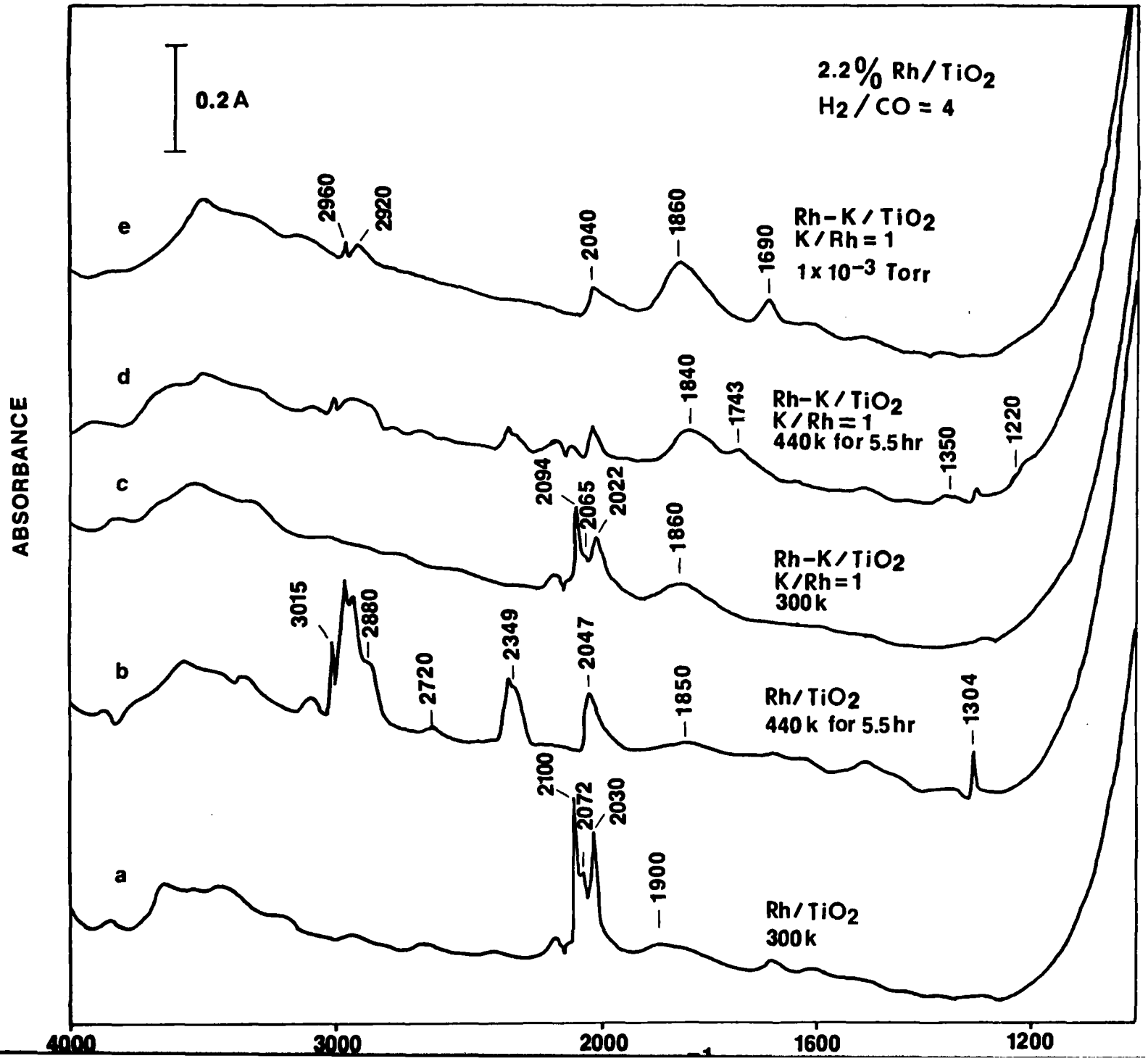
0.2 A
2.2% Rh/TiO2
H2/CO = 4
ABSORBANCE
e
2960
2920
2040
1860
1690
Rh-K/TiO2
K/Rh = 1
1x10-3 Torr
d
1840
1743
1350
1220
Rh-K/TiO2
K/Rh = 1
440k for 5.5hr
c
2094
2065
2022
1860
Rh-K/TiO2
K/Rh = 1
300k
b
3015
2880
2720
2349
2047
1850
1304
Rh/TiO2
440k for 5.5hr
a
2100
2072
2030
1900
Rh/TiO2
300k
4000
3000
2000
1600
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