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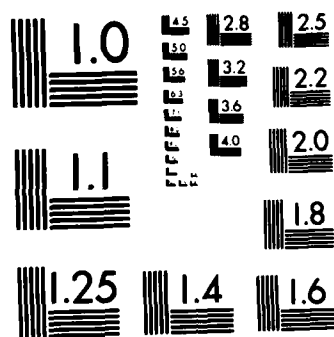
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THE EFFECT OF POTASSIUM ON THE HYDROGENATION OF CO
AND CO₂ OVER SUPPORTED Rh CATALYSTS

BY

S. D. Worley and C. H. Dai
Department of Chemistry
Auburn University
Auburn University, AL 36849

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The Effect of Potassium on the Hydrogenation of CO and CO₂ over Supported Rh Catalysts

S.D. Worley and C.H. Dai

Department of Chemistry, Auburn University, Auburn, AL 36849

The reactions of hydrogen with carbon monoxide and carbon dioxide over Rh/Al₂O₃ and Rh/TiO₂ films, some of which contained potassium as an additive, have been investigated. For the CO hydrogenation reaction the presence of potassium caused the dissociation or desorption of the gem dicarbonyl, linear CO, and carbonyl hydride species, while it led to an enhancement of the bridged carbonyl species. For Rh/TiO₂ films the hydrogenation of CO produced acetone and acetaldehyde as oxygenated products; the bridged carbonyl species was the likely precursor of these products. For the CO₂ hydrogenation reaction the presence of potassium caused the dissociation or desorption of all CO species, and oxygenated products were not produced. Potassium significantly poisoned both reactions toward the production of methane.



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Considerable effort has been expended here toward the investigation of the CO and CO₂ hydrogenation reactions over supported Rh catalysts (1-4). Although for Rh/X (X = Al₂O₃ and TiO₂) at low pressure (50-100 Torr) and temperature (423-473 K) the predominant product for both of these reactions is methane (1-4), there are means of altering the product distribution toward higher hydrocarbons and/or oxygenated products such as methanol. In general it is believed that methane and higher hydrocarbons are produced from dissociated CO or CO₂ on supported transition metals, while undissociated CO is thought to be a precursor to oxygenated products (5). Basic support materials such as ZnO, MgO, La₂O₃, and ZrO₂ (6,7) as well as higher pressure (over 1 atm) (8,9) seem to shift the product selectivity toward oxygenates; however, Al₂O₃ and TiO₂ as support materials can also lead to oxygenated products under special conditions. For example, Goodwin and coworkers (5) have shown recently that added potassium causes the selectivity for hydrogenation of CO over 3% Rh/TiO₂ to shift toward oxygenated products with acetaldehyde and acetone being present in significant quantities. There has been considerable recent interest in the effects of alkali metals on catalytic reactions over single crystals (10) and over supported transition metals (5,11). This paper will report the results of recent work in these laboratories concerning the effects of potassium on the CO and CO₂ hydrogenation reactions over supported Rh catalytic films.

Experimental

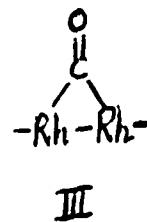
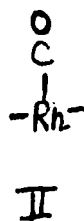
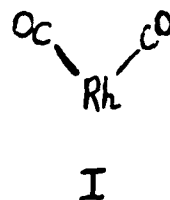
The Rh/Al₂O₃ and Rh/TiO₂ catalysts used in this study were prepared in a manner similar to those studied previously here (1-4,12). Briefly, acetone/water solutions containing appropriate amounts of RhCl₃·3H₂O, KCl,

and alumina (Degussa Aluminum Oxide C, $100 \text{ m}^2 \text{g}^{-1}$ or titania (Degussa Titanium Dioxide P25, $50 \text{ m}^2 \text{g}^{-1}$) were 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 (2-4) which was evacuated overnight. The sample film was then evacuated at 470 K for 1 hr, 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 $\text{CO}:\text{H}_2$ or $\text{CO}_2:\text{H}_2$ 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 reactions were monitored by infrared spectroscopy (Perkin Elmer 983 with data system) (1-4); 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 (± 0.01 Torr).

Results and Discussion

CO Hydrogenation

The interaction of CO with supported Rh catalysts has been well characterized by infrared spectroscopy (13). The primary surface species obtained are shown below. The "gem dicarbonyl" species (I) exhibits two



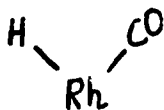
sharp infrared bands at ca. 2030 and 2100 cm^{-1} which do not generally shift in wavenumber with changing surface coverage. This indicates that dipolar coupling of nearby adsorbed CO molecules is minimal for supported Rh containing predominantly this species. For Rh/X (X = Al_2O_3 , TiO_2 , or SiO_2) catalysts containing less than 1% by weight Rh, species I is the only species detected by infrared. The facts that the infrared bands for species I do not shift with coverage and that no other CO species are detected for catalysts containing low Rh loading have led some workers to suggest that species I refers to Rh in a highly dispersed state, possibly even isolated Rh atoms(12,13). Work in several laboratories (12-14) has established that Rh in species I exists in the +1 oxidation state; this probably also contributes to its tendency to remain highly dispersed. Recent work has shown that the dispersion of Rh ions in species I may be actually caused by the presence of adsorbed CO (15,16).

Figures 1 and 2 illustrate the effect of potassium on species I for a 0.5% Rh/ Al_2O_3 catalyst film. In this experiment the two catalysts were treated identically. They were held successively at temperatures of 300, 320, 380, 430, and 460 K for 30 min at each temperature in the presence of 1×10^{-3} Torr of CO. The infrared band intensities were very similar through 380 K, probably indicating comparable CO coverages for the two samples. However, after 30 min at 430 K species I disappeared for the sample containing potassium (K: Rh = 2:1), but this phenomenon did not occur until after 30 min heating at 460 K for the sample which did not

contain potassium. Clearly potassium did not significantly block species I sites; rather it functioned to aid either CO bond dissociation or CO desorption from the surface, most probably through an electronic effect. The potassium may well be located on the support in close proximity to Rh^+ sites. Some workers have observed K/CO interactions on single crystals (17). Such interactions can give rise to low frequency CO infrared bands ($1400\text{--}1800\text{ cm}^{-1}$). A comparison of Figs. 1 and 2 indicates that such interactions do not occur appreciably for 0.5% $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts which suggests that the K/CO interaction which causes enhanced dissociation or desorption of CO on or from Rh in species I may be one of long range.

When Rh/X catalysts containing higher Rh loadings ($>1\%$) are employed, in addition to species I generally two other CO species can be detected by infrared. Species II, the "linear" species, contains one CO molecule adsorbed on a Rh atom, while species III, the "bridged carbonyl" species, contains CO bridged across two Rh atoms (13). The infrared bands for these two species shift to higher wavenumber as the CO surface coverage is increased leading most workers to suggest that these two species correspond to clusters of Rh atoms rather than highly dispersed ions as for species I. Figure 3 shows a comparison of the behavior of the CO hydrogenation reaction over 2.2% Rh/TiO_2 catalyst films with and without the presence of potassium. In spectrum 3a for a sample containing no potassium the four infrared bands normally observed are in evidence; the 2100 and 2030 cm^{-1} bands correspond to species I, while the 2072 cm^{-1} band and the broad band near 1900 cm^{-1} can be assigned to species II and III, respectively. Upon heating at 440 K for 5.5 hr (spectrum 3b), species I and II disappeared, a new band was detected at 2047 cm^{-1} , the species III band declined in intensity, and bands corresponding to gas phase methane ($3015, 1304\text{ cm}^{-1}$)

and carbon dioxide (2349 cm^{-1}) were produced. The band at 2047 cm^{-1} corresponds to a carbonyl hydride species rather than species II.



The carbonyl hydride species for supported Rh was first suggested by Solymosi and coworkers (18) and later confirmed by isotopic labeling studies here (3,4). Upon addition of potassium at 300 K (Fig. 3c), all infrared bands except the broad band for species III declined in intensity. Upon heating at 440 K for 5.5 hr (Fig. 3d), the infrared bands for species I, II, the carbonyl hydride, methane, and carbon dioxide all declined markedly in intensity relative to the identical treatment for the sample containing no potassium. Only the species III band became considerably more intense. Weak new bands at 1743 , 1350 , and 1220 cm^{-1} which vanish upon evacuation (Fig. 3e) can be attributed to the formation of acetone; this has been confirmed by gas chromatography. Table I shows the product distributions for these experiments. Acetone and acetaldehyde were produced as oxygenated products over Rh/TiO₂ and to a greater extent when potassium was present. Similar results were observed for 2.2% Rh/Al₂O₃, *ie.* enhanced species III (although to less extent than noted for Rh/TiO₂), less species I, II, and carbonyl hydride when potassium was present; however, oxygenated products were not detected for Al₂O₃ as the support. Goodwin and coworkers (5) have also observed the production of comparable amounts of acetone and acetaldehyde over potassium-doped Rh/TiO₂ (K:Rh =

Table I. Product Distribution for CO Hydrogenation.

	TN(CH ₄) ^a	Mole Percents					
		CO ₂	CH ₄	C ₂ H ₆	CnHm n>2	CH ₃ CHO	CH ₃ COCH ₃
2.2%Rh/Al ₂ O ₃	1.23x10 ⁻⁴	15.8	64.0	10.4	9.9	-----	-----
2.2%Rh-K/Al ₂ O ₃ K/Rh=1	1.63x10 ⁻⁵	33.3	66.6	-----	-----	-----	-----
2.2%Rh/TiO ₂	4.20x10 ⁻⁴	32.0	51.3	4.7	2.4	6.7	2.9
2.2%Rh-K/TiO ₂ K/Rh=1	4.92x10 ⁻⁵	25.7	42.8	8.6	0.1	10.8	12.2

^a Turnover number for production of methane (molecules/Rh atom/sec).

1:2) although their reaction conditions were quite different (523 - 708 K, 1 - 10 atm, $\text{CO:H}_2 = 2:1$) than those here.

It is generally thought that oxygenated products in the CO hydrogenation reaction result from reaction of undissociated CO with hydrocarbon fragments (5). Since the presence of potassium appears to enhance the formation of the bridged carbonyl species III at the expense of the other species, it is likely that the bridged species is the precursor to the oxygenated products. The gem dicarbonyl species I and linear CO species II most likely dissociate at low temperature to form carbon and the carbonyl hydride species when hydrogen is present. The hydride ligand causes further dissociation of CO due to back donation of electron density into the π^* orbital of CO. Hydrogenation of active carbon then leads to the production of methane and higher hydrocarbons. Potassium must function in several roles. It poisons the methanation reaction either by site blockage for species I, II, and the carbonyl hydride or by accelerating the production of inactive carbon through an electronic effect (electron donation into the π^* orbital of CO). Furthermore, it accentuates the production of species III probably by steric blockage of species I and II thus enhancing the concentration of undissociated CO which can form oxygenated products.

CO₂ Hydrogenation

The hydrogenation of CO₂ does not produce CO species I, II, and III in infrared detectable amounts. It does produce the carbonyl hydride species thus proving that CO₂ is dissociated over supported Rh (2-4). Figure 4 illustrates the behavior of a 2.2% Rh/Al₂O₃ catalyst for a series of experiments in which samples having different potassium loadings are heated

at 440 K for 5.5 hr. Note that the infrared band at $2020-2040\text{ cm}^{-1}$ for the carbonyl hydride species is absent for all spectra shown; it was present at 300 K for the sample having no potassium, but it was greatly diminished in intensity at 300 K for the samples containing potassium, and it vanished at 300 K when the K:Rh ratio was 1.0. It is evident in the spectra shown in Fig. 4 that the amount of methane produced declined as the K:Rh ratio was increased; also, there was no spectroscopic evidence for oxygenated products.

Figure 5 shows the analogous results for CO_2 hydrogenation over a 2.2 % Rh/ TiO_2 film which contained either no potassium (Fig. 5a,b) or K:Rh = 2.0 (Fig. 5c,d). The carbonyl hydride species was present (2037 cm^{-1}) for the sample containing no potassium, but it was absent even at room temperature for the sample containing potassium. The methanation activity was substantially decreased when potassium was present, and no oxygenated products were detected by infrared or by gas chromatography (Table II). The data in Table II show that the turnover number for methane production for CO_2 hydrogenation was higher in all cases for Rh/ TiO_2 than for Rh/ Al_2O_3 , and that potassium poisoned the methanation reaction for both types of supported catalysts. Figure 6 shows that the poisoning effect was linear for both supports, but a larger slope illustrates that the effect of potassium as an additive was more dramatic for TiO_2 . The poisoning effect was exponential as a function of potassium loading for 0.5% Rh/ Al_2O_3 .

Infrared spectroscopy indicates that there is very little CO adsorbed intact on Rh during the hydrogenation of CO_2 . Evidently the CO_2 dissociates rapidly on the supported Rh catalysts to produce active carbon which is subsequently hydrogenated to methane and a smaller amount of higher hydrocarbons. The presence of potassium during the hydrogenation of

Table II. Product Distribution for CO₂ Hydrogenation.

	2.2% Rh-K/Al ₂ O ₃			2.2% Rh-K/TiO ₂		
	CH ₄	C ₂ H ₆	TN(CH ₄) ^a	CH ₄	C ₂ H ₆	TN(CH ₄) ^a
K/Rh=0.0	89.0 ^b	11.0 ^b	3.61x10 ⁻⁴	97.6 ^b	2.4 ^b	1.48x10 ⁻³
K/Rh=0.5	87.3	12.4	2.09x10 ⁻⁴	96.7 ^b	3.3	1.37x10 ⁻³
K/Rh=1.0	86.4	13.6	1.62x10 ⁻⁴	95.9	4.0	9.50x10 ⁻⁴
K/Rh=1.2	ND	ND	ND	94.5	5.5	7.98x10 ⁻⁴
K/Rh=1.5	86.4	13.6	1.49x10 ⁻⁴	92.0	8.0	4.32x10 ⁻⁴
K/Rh=2.0	ND	ND	5.82x10 ⁻⁵	ND	ND	2.16x10 ⁻⁴

^a Turnover number for production of methane (molecules/Rh atom/sec).

^b Mole percents.

ND No determination.

CO_2 does not cause an enhanced formation of bridged carbonyl species III as was the case for CO hydrogenation. Thus no oxygenated products are observed. Potassium probably poisons the methanation reaction by site blockage and by enhancing dissociation of CO_2 to inactive carbon.

Conclusions

Potassium poisons the methanation reaction for both CO and CO_2 hydrogenation over supported rhodium. For CO hydrogenation it causes an enhanced amount of bridged species III which is not dissociated and is probably the precursor of the oxygenated products acetone and acetaldehyde. For CO_2 hydrogenation CO species can not be detected during the reaction when potassium is present, and oxygenated products are not detected. The effect of potassium is more dramatic for CO_2 hydrogenation over Rh/TiO₂ than over Rh/Al₂O₃.

Acknowledgments

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Figure Captions

Figure 1. Infrared spectra for the interaction of CO with a 0.5% Rh/Al₂O₃ film (4.0 mg cm⁻²) at a background pressure of 1×10^{-3} Torr as a function of temperature.

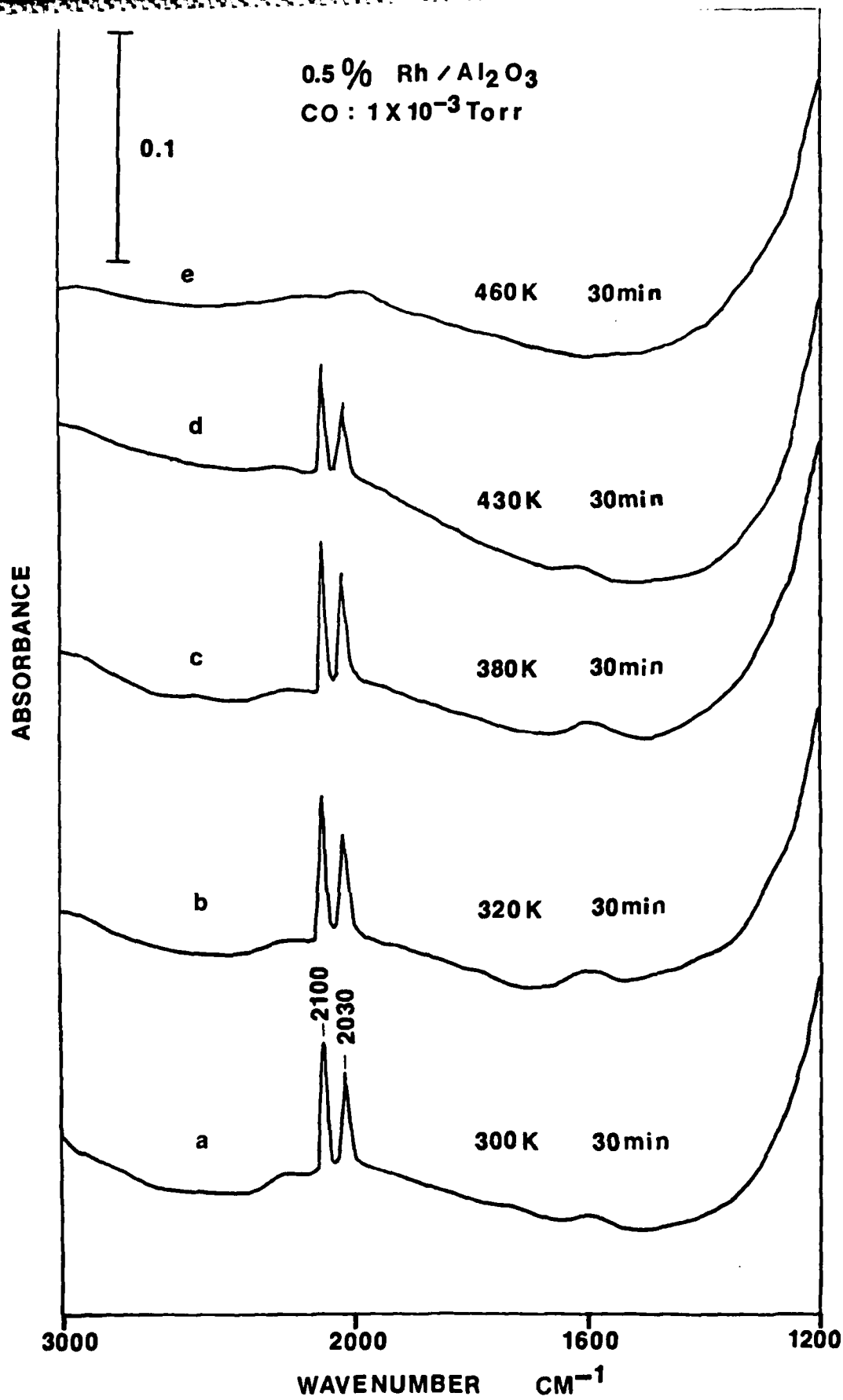
Figure 2. Infrared spectra for the interaction of CO with a 0.5% Rh/Al₂O₃ film (4.0 mg cm⁻²) to which has been added potassium at K:Rh ratio of 2:1 at a background pressure of 1×10^{-3} Torr as a function of temperature.

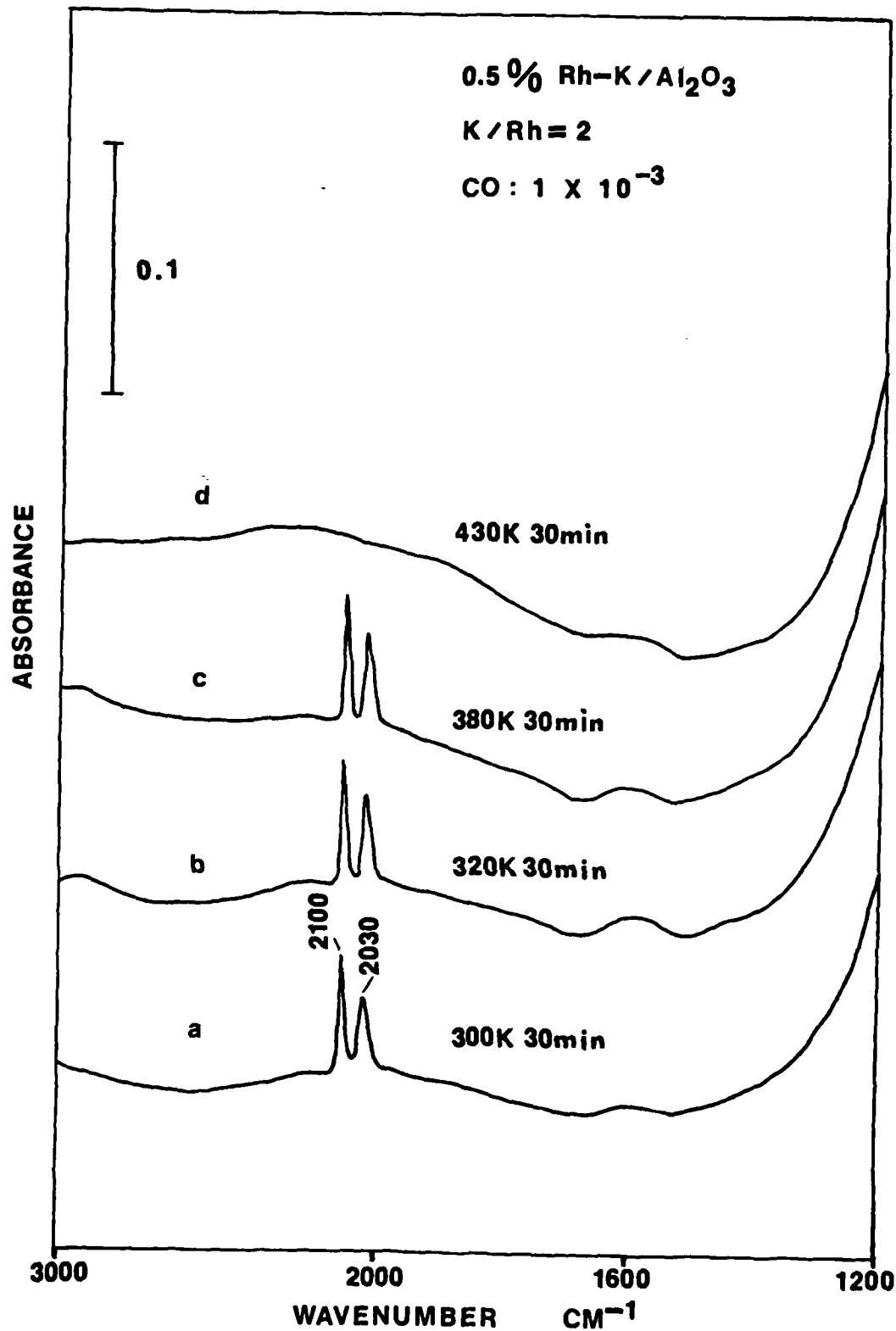
Figure 3. Infrared spectra for the interaction of H₂ and CO over 2.2% Rh/TiO₂ films (4.3 mg cm⁻²) with or without potassium added as indicated; total pressure was 82.5 Torr.

Figure 4. Infrared spectra for the interaction of H₂ and CO₂ over 2.2% Rh/Al₂O₃ films (4.3 mg cm⁻²) as a function of concentration of potassium as an additive; total pressure was 82.5 Torr.

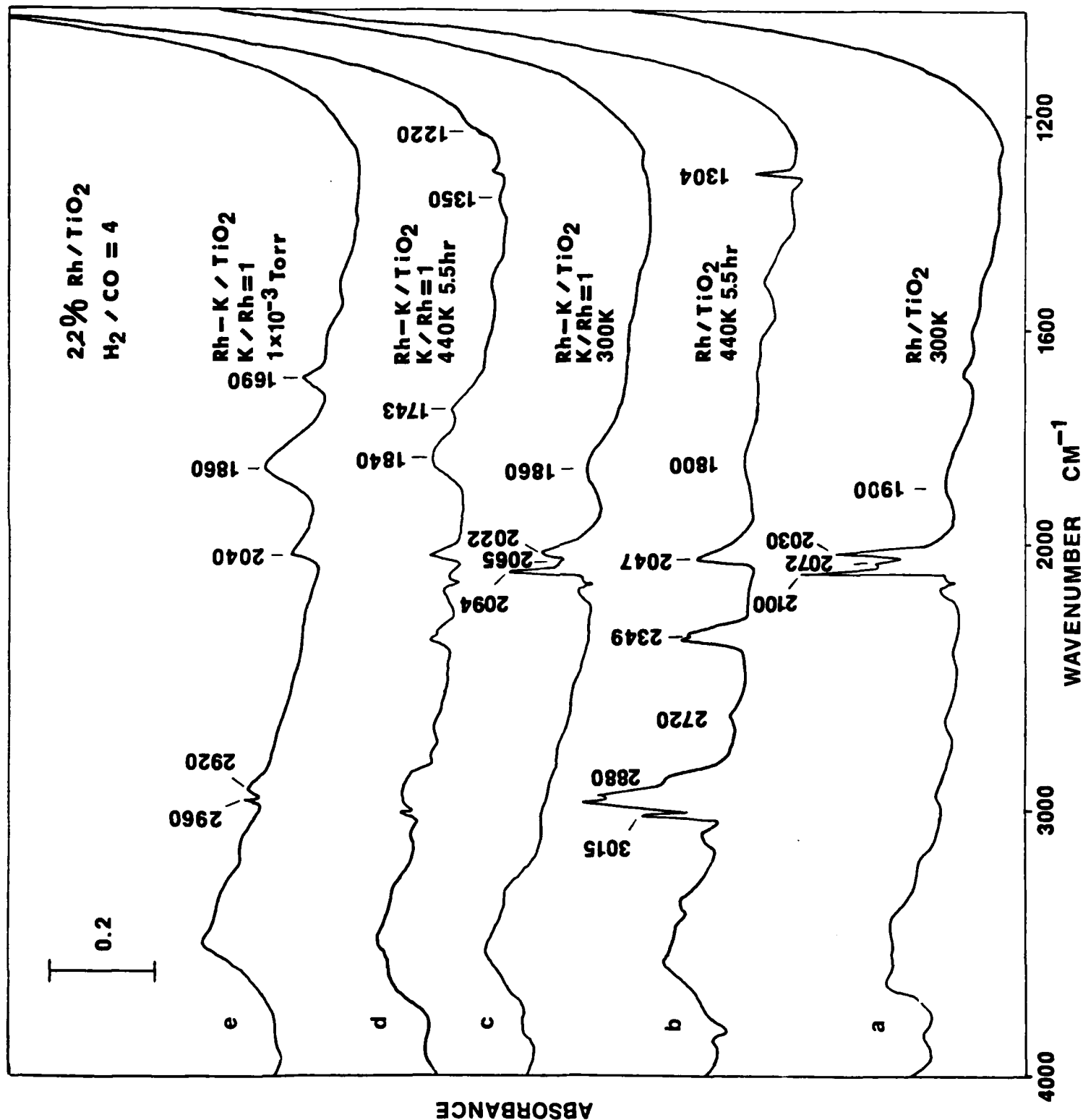
Figure 5. Infrared spectra for the interaction of H₂ and CO₂ over 2.2% Rh/TiO₂ films (4.3 mg cm⁻²) with or without potassium added as indicated; total pressure was 82.5 Torr.

Figure 6. Turnover number for CH₄ production as a function of concentration of potassium as an additive over 2.2% Rh/X (X = Al₂O₃, TiO₂) films (4.3 mg cm⁻²); total pressure was 82.5 Torr, and reaction temperature was 440 K.

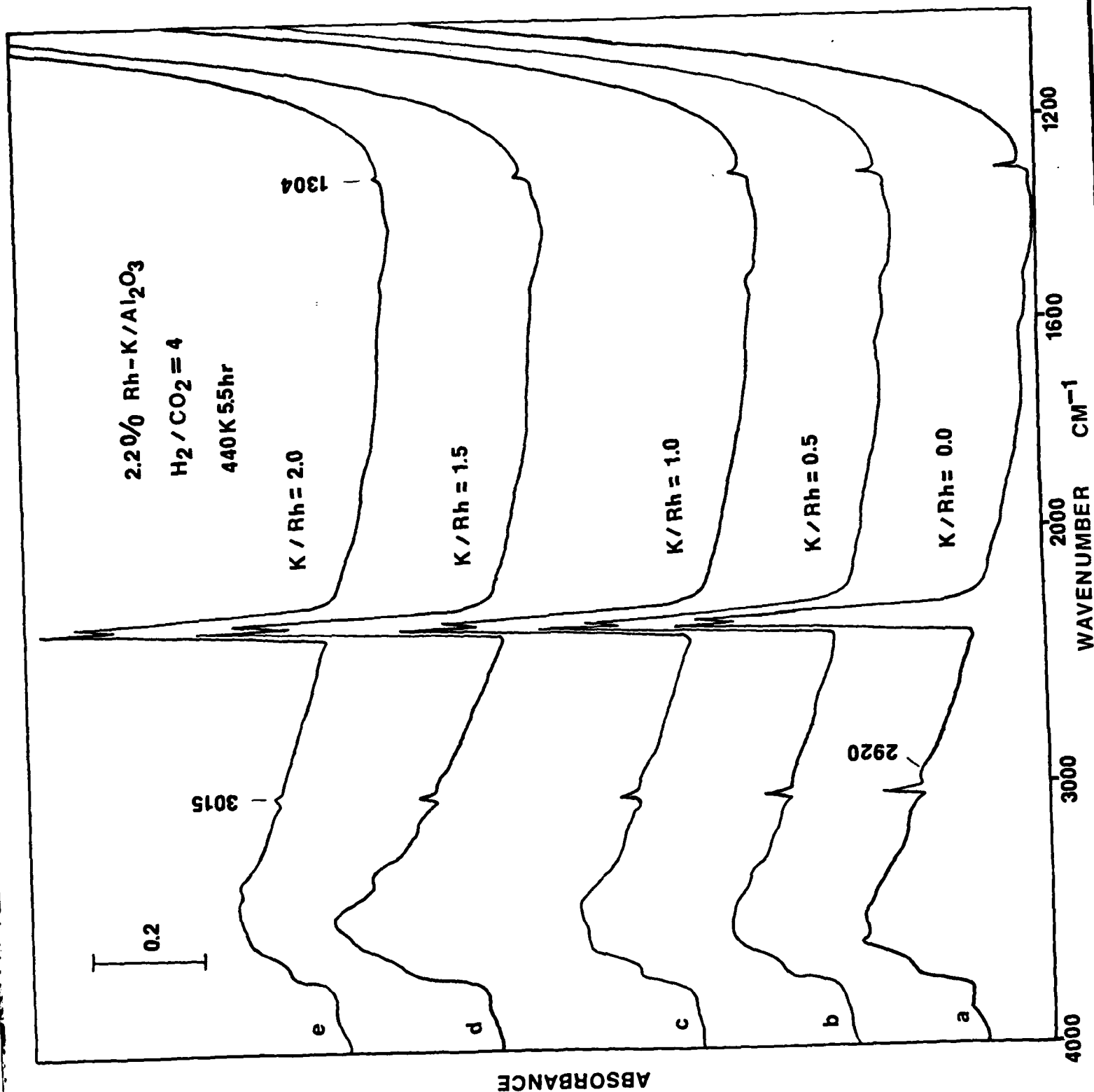




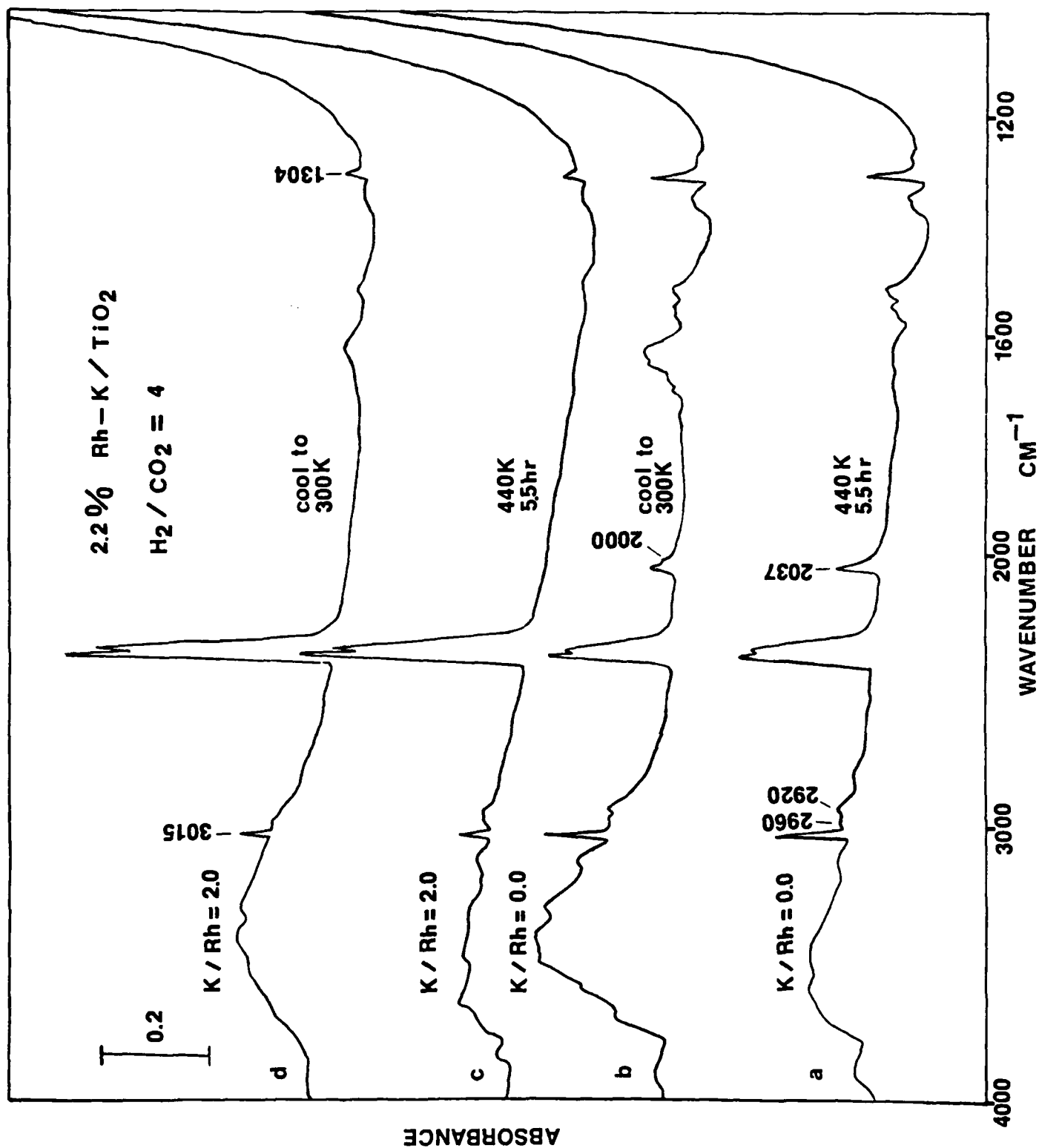
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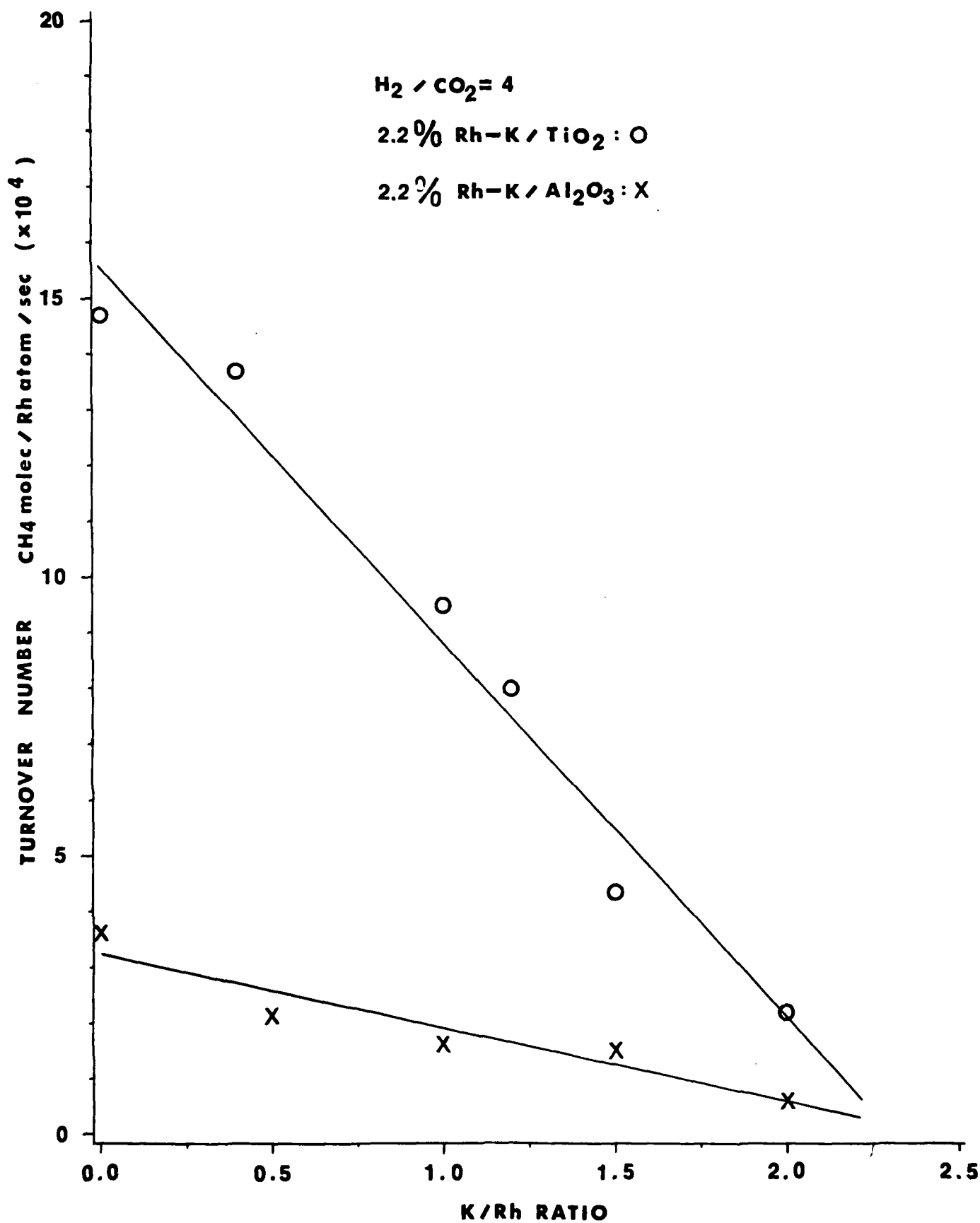
Worley et al., Fig. 3



Wong & Bai, Fig. 4



Worley & Bai, Fig. 5



1000, 400, Fig. 6

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University of Oklahoma
Norman, Oklahoma 73019

Dr. Aaron Fletcher
Code 3852
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. J. Cooper
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

Dr. M. C. Baird
Department of Chemistry
Queen's University
Kingston, Canada
K7L 3N6

Dr. N. N. Lichtin
Department of Chemistry
Boston University
685 Commonwealth Avenue
Boston, Massachusetts 02215

Dr. R. Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627

Dr. N. Cooper
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

~~Dr. S. D. Worley
Department of Chemistry
Auburn University
Auburn, Alabama 36830~~

Dr. L. Vaska
Department of Chemistry
Clarkson College
Potsdam, New York 13676

Dr. R. A. Huggins
Materials Science and
Engineering Department
Stanford University
Stanford, California 94305

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