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DECOMPOSITION OF METHANOL ACETALDEHYDE AND ACETONE ON  
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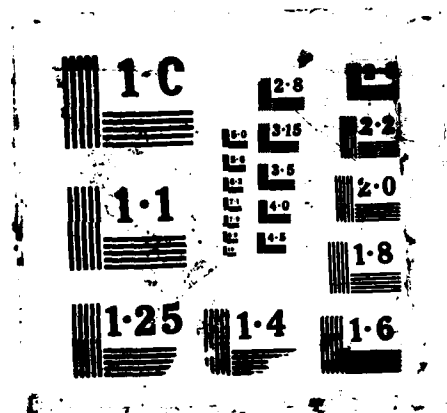
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DECOMPOSITION OF METHANOL, ACETALDEHYDE, AND ACETONE  
ON SUPPORTED RHODIUM CATALYSTS

BY

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

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## REPORT DOCUMENTATION PAGE

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>The decomposition processes for methanol, acetaldehyde, and acetone over supported rhodium catalytic films have been investigated using infrared spectroscopy. An interesting support effect was observed for methanol decomposition with methane being the primary product over Rh/TiO <sub>2</sub> <sup>n</sup> and dimethyl ether being formed over Rh/Al <sub>2</sub> O <sub>3</sub> <sup>n</sup> . In the latter case the Al <sub>2</sub> O <sub>3</sub> <sup>n</sup> support was the active catalyst. For acetaldehyde decomposition the principle products were methane and acetone for both supported rhodium catalysts. Acetone decomposition produced only inactive carbon with no other infrared-detectable surface species. It is possible that a metallic rhodium gem dicarbonyl adsorbate was produced during the decomposition of acetaldehyde over Rh/Al <sub>2</sub> O <sub>3</sub> <sup>n</sup> . Previous observations of the rhodium gem dicarbonyl species have referred to dispersed Rh <sub>u</sub> ions. |       |                                                      |                                                                                                                                                                               |                                                 |                    |
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Decomposition of Methanol, Acetaldehyde, and Acetone on Supported Rhodium Catalysts

C.H. Dai and S.D. Worley\*

Department of Chemistry, Auburn University, AL 36849

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### Abstract

The decomposition processes for methanol, acetaldehyde, and acetone over supported rhodium catalytic films have been investigated using infrared spectroscopy. An interesting support effect was observed for methanol decomposition with methane being the primary product over  $\text{Rh/TiO}_2$  and dimethyl ether being formed over  $\text{Rh/Al}_2\text{O}_3$ . In the latter case the  $\text{Al}_2\text{O}_3$  support was the active catalyst. For acetaldehyde decomposition the principle products were methane and acetone for both supported rhodium catalysts. Acetone decomposition produced only inactive carbon with no other infrared-detectable surface species. It is possible that a metallic rhodium gem dicarbonyl adsorbate was produced during the decomposition of acetaldehyde over  $\text{Rh/Al}_2\text{O}_3$ . Previous observations of the rhodium gem dicarbonyl species have referred to dispersed  $\text{Rh}^+$  ions.

## Introduction

A considerable amount of work has been performed in these laboratories and elsewhere focused upon the elucidation of the mechanisms for the hydrogenation reactions of CO and CO<sub>2</sub> over supported rhodium catalysts.<sup>1</sup> The product distributions for these two reactions depend markedly upon the reaction conditions, with variables including (at least) temperature, pressure, nature of the support, and the presence or absence of alkali metal promoters. For example, a recent study of CO hydrogenation over Rh/TiO<sub>2</sub> showed that the presence of potassium ions poisoned the methanation reaction, but enhanced the yield of the oxygenated products acetaldehyde and acetone.<sup>2</sup> Our interest is currently directed toward the detection of intermediates in the hydrogenation reactions mentioned above using infrared spectroscopy as a primary analytical probe. We have been able to detect a rhodium carbonyl hydride species during the production of methane and higher hydrocarbons<sup>1,3,4</sup> in accord with the previous work of Solymosi and coworkers.<sup>5-8</sup> We now wish to extend our work to the detection of intermediates leading to the oxygenated products. The current paper will describe our observations concerning the reverse processes (decomposition of methanol, acetaldehyde, and acetone over supported rhodium catalyst films). The decomposition reactions of methanol over Rh(111)<sup>9</sup> and on the supports employed here<sup>10-14</sup> have been investigated previously, but not by using the infrared cell-reactor techniques employed in these laboratories.

## Experimental Section

The catalytic sample preparation procedure developed here for Rh/TiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> films has been described elsewhere<sup>1-4</sup> but will be reiterated briefly here. Slurries of RhCl<sub>3</sub>·3H<sub>2</sub>O, support material (Degussa Titanium Dioxide P25, 50 m<sup>2</sup>g<sup>-1</sup> or Degussa Aluminum Oxide C, 100 m<sup>2</sup>g<sup>-1</sup>), in some cases KCl, and

water/acetone were sprayed from an atomizer onto a 25 mm  $\text{CaF}_2$  infrared window held at ca. 360 K. Evaporation of the solvents left a thin film (ca. 4.3 mg  $\text{cm}^{-2}$ ) of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TiO}_2$  (or  $\text{Al}_2\text{O}_3$ ), which in some runs contained potassium ions, adhered to the  $\text{CaF}_2$  window. The window containing the catalytic film was mounted inside a Pyrex infrared cell reactor<sup>1</sup> which was then evacuated to  $10^{-6}$  Torr using an ion pump. The sample was reduced by 85 Torr doses of hydrogen at 480 K for periods of 5, 5, 10, and 20 min, each reduction cycle being followed by evacuation. Prior studies in these laboratories and elsewhere have shown that this procedure provides a mixture of isolated  $\text{Rh}^+$  ions and  $\text{Rh}^0$  clusters; the  $\text{Cl}^-$  is lost as  $\text{HCl}$ . Following heating for 1 h at 490 K under vacuum, the samples were evacuated overnight to  $10^{-6}$  Torr at ambient temperature. Then 20.0 Torr of either methanol, acetaldehyde, or acetone was introduced into the cell reactor. These materials had been purified by repetitive freeze-thaw evacuation cycles. After recording the infrared spectrum (Perkin-Elmer 983 with data system) at 300 K, the catalyst sample was brought to 440 K, and the infrared spectra were monitored as a function of time. Gaseous products were analyzed at the conclusion of the experiments using chromatography (Carle 400). Pressure measurements were made with an MKS Baratron capacitance manometer ( $\pm 0.01$  Torr). Runs involving support material only were made using the same general procedure.

## Results and Discussion

Figures 1 and 2 show the infrared spectra for the methanol decomposition process over 2.2%  $\text{Rh}/\text{TiO}_2$  and 2.2%  $\text{Rh}/\text{Al}_2\text{O}_3$ , respectively. A comparison of the analogous spectra in the two figures reveals that there was a significant support effect. Spectrum 1a shows that even at ambient temperature the  $\text{Rh}/\text{TiO}_2$  film began to catalyze the decomposition of methanol, as some adsorbed

CO features were detected near  $2000\text{ cm}^{-1}$  which overlap the C-O stretching overtone band<sup>15</sup> for  $\text{CH}_3\text{OH}$  (2035, P; 2056, Q; 2078, R). Heating for 1.5 h at 440 K (Fig. 1b) caused significant decomposition as evidenced by the declination of band intensity in the C-H stretch region ( $2850$  and  $2950\text{ cm}^{-1}$ ) and the CO stretch region (1012, P; 1034, Q; 1060, R)<sup>15</sup>, with a concomitant enhancement of the adsorbed CO bands in the range  $1850$ - $2120\text{ cm}^{-1}$ . Based upon extensive prior work in these laboratories,<sup>1,16,17</sup> these bands can be assigned to CO stretching modes as follows: 1850, bridged dirhodium carbonyl; 1975, carbonyl bridged between Rh and the support  $\text{TiO}_2$ ; 2037, the rhodium carbonyl hydride species; 2050, a "linear CO" rhodium species; 2120, CO adsorbed on  $\text{Rh}^{+2}$  (or at least in an oxidation state higher than +1)<sup>16,18</sup>. It is interesting that there was no evidence of sharp twin bands at 2030 and  $2100\text{ cm}^{-1}$  indicating that the isolated  $\text{Rh}^{+1}$  "gem dicarbonyl" species was not formed during the decomposition of methanol. It is well known that CO gas causes disruption of Rh clusters to produce highly dispersed  $\text{Rh}^{+1}$  sites,<sup>19,20</sup> but evidently methanol is not capable of causing similar behavior. Figure 1c shows the result of further decomposition at 440 K (after 5.5 h); the bands attributed to methanol and CO surface species have greatly declined in intensity, and those present at  $1304/3015\text{ cm}^{-1}$  and  $2349\text{ cm}^{-1}$  indicate the formation of gas-phase methane and carbon dioxide. Analysis by gas chromatography indicated that at this point the gas-phase methanol was completely decomposed. Comparison with spectrum 1e indicates that under the same reaction conditions  $\text{TiO}_2$  alone causes some decomposition of  $\text{CH}_3\text{OH}$ , but no  $\text{CH}_4$ ,  $\text{CO}_2$ , or CO surface species were detected. It is clear that Rh plays an active role in the decomposition of  $\text{CH}_3\text{OH}$  when  $\text{TiO}_2$  is the support. Spectrum 1d shows the result of adding potassium ions ( $\text{K}:\text{Rh}=1$ ) to the 2.2% Rh/ $\text{TiO}_2$  catalyst. This caused a substantial decrease in the rate of decomposition of

$\text{CH}_3\text{OH}$  (86% decomposition indicated by GC), an elimination of  $\text{CH}_4$  as a product, and a decline in the production of  $\text{CO}_2$  and most adsorbed CO species. However, the bridged dirhodium carbonyl species was significantly enhanced. The increase of this CO species of Rh and the poisoning of the methanation reaction in the presence of potassium ions has been noted previously for the hydrogenation of CO and  $\text{CO}_2$  over supported rhodium films.<sup>2</sup>

In contrast to the results noted for 2.2% Rh/ $\text{TiO}_2$  above, for the 2.2% Rh/ $\text{Al}_2\text{O}_3$  catalyst only the rhodium carbonyl hydride and bridged dirhodium carbonyl adsorbed CO species were produced in significant amounts (Fig. 2b, c), no decomposition occurred at 300 K,  $\text{CH}_4$  and  $\text{CO}_2$  were not produced in significant amounts, and the primary decomposition product was dimethyl ether (bands at 1180 and 1110  $\text{cm}^{-1}$ , verified by gas chromatography). However, a comparison of spectra 2c and 2e indicates that the dimethyl ether production is catalyzed primarily by the  $\text{Al}_2\text{O}_3$  support rather than by rhodium. Spectrum 2d shows that the presence of potassium ions poisons the production of dimethyl ether indicating that the  $\text{K}^+$  is spread over the support as well as on Rh. The  $\text{K}^+$  ions must also interact with Rh because the carbonyl hydride species was diminished, and the bridged dirhodium carbonyl species was enhanced when potassium was present. We would postulate that the potassium poisons the active Rh methanation sites by aiding the formation of inactive carbon on these sites and enhancing the formation of the bridged dirhodium carbonyl species, which we have noted before does not yield methane under the conditions (440 K and low pressure) of our experiments.<sup>2</sup> As noted before, the potassium ions also poison the production of dimethyl ether on the  $\text{Al}_2\text{O}_3$  support. This is probably a result of blockage of Lewis acid sites, as pointed out by Busca *et al.* in their studies of the interaction of methanol with KOH doped  $\text{TiO}_2$ .<sup>14</sup>

Thus it might be postulated that under the conditions of our experiments, Rh/TiO<sub>2</sub> catalyzes the rupture of the C-O bond in methanol to produce active carbon (CH<sub>3</sub>) which subsequently leads to CH<sub>4</sub> and CO<sub>2</sub>, as products, while Rh/Al<sub>2</sub>O<sub>3</sub> assists the rupture of the O-H bond in methanol as well to form CH<sub>3</sub>O which subsequently leads to the production of dimethyl ether. In the latter case the Rh performs little useful purpose with the Al<sub>2</sub>O<sub>3</sub> providing the catalysis.

Figures 3 and 4 present the infrared spectra for the decomposition of acetaldehyde over 2.2% Rh/TiO<sub>2</sub> and 2.2% Rh/Al<sub>2</sub>O<sub>3</sub>, respectively. In this case the results were similar for the two different supported catalysts. Spectrum 3a indicates that little acetaldehyde decomposed at 300 K, but upon heating at 440 K (spectra 3b,c), marked decomposition occurred (85% as measured by GC) to form CH<sub>4</sub> (1304 cm<sup>-1</sup>), CO<sub>2</sub> (2349 cm<sup>-1</sup>), CO (2143 cm<sup>-1</sup>), adsorbed bridged rhodium carbonyl species (1800-2000 cm<sup>-1</sup>), surface carbonate and acetate species (1410, 1445, 1526, 1576 cm<sup>-1</sup>), and acetone (1240, 1340 cm<sup>-1</sup>). Decomposition occurred over the pure TiO<sub>2</sub> support material also (Fig. 3e), but only surface acetate bands were observed. Thus it can be concluded that the acetate species was confined primarily to the TiO<sub>2</sub> support. It should be noted that Orita *et al.* have detected adsorbed acetate ions during the formation of acetaldehyde from the hydrogenation of CO over Rh/SiO<sub>2</sub>.<sup>21</sup> Prior work in these laboratories suggested that acetaldehyde and acetone were produced from the bridged dirhodium carbonyl species during the hydrogenation of CO over 2.2% Rh/TiO<sub>2</sub>, while methane was produced from the other adsorbed CO species.<sup>2</sup> Spectrum 3c shows that the only adsorbed CO/Rh species produced during the decomposition of acetaldehyde was the bridged carbonyl species. Spectrum 3d indicates that the presence of potassium ions poisoned, to some extent, the decomposition of acetaldehyde (reduced to 54%) and eliminated the

formation of  $\text{CH}_4$  and acetone. Most likely the potassium ions cause the formation of inactive carbon at the expense of the active carbon surface species which normally yield hydrocarbon and oxygenated products.

Figure 4 shows that the decomposition of acetaldehyde over 2.2%  $\text{Rh}/\text{Al}_2\text{O}_3$  again produced  $\text{CH}_4$ , although very little  $\text{CO}_2$  or  $\text{CO}$ , surface acetate, and acetone. Spectrum 4e indicates that the acetate species was primarily confined to the  $\text{Al}_2\text{O}_3$  support. Again potassium ions (spectrum 4d) poisoned the production of  $\text{CH}_4$  and acetone. The most interesting feature appears in spectrum 4b. Upon initial heating at 440 K, twin adsorbed CO bands occurred at 2012 and 2082  $\text{cm}^{-1}$ . It is well known<sup>16</sup> that the presence of sharp twin bands which grow and decline in intensity together in this region of the spectrum are indicative of the presence of a rhodium gem dicarbonyl species. However, it is also a fact that these twin bands generally appear at ca. 2030 and 2100  $\text{cm}^{-1}$  and refer to a highly dispersed  $\text{Rh}^+$  gem dicarbonyl.<sup>16</sup> The gem dicarbonyl bands in spectrum 4b which do grow proportionately appear 18  $\text{cm}^{-1}$  lower which could very well mean that acetaldehyde decomposes over  $\text{Rh}/\text{Al}_2\text{O}_3$  to yield a rhodium gem dicarbonyl species with Rh in a zero oxidation state. If so, to our knowledge, this is the first infrared data which has been interpreted as evidence for the existence of a metallic Rh gem dicarbonyl species. Yates and Cavanagh also observed abnormally low frequency infrared bands (2021 and 2088  $\text{cm}^{-1}$ ) for a Rh gem dicarbonyl species during the decomposition of formaldehyde over 2.2%  $\text{Rh}/\text{Al}_2\text{O}_3$ , but they attributed the low frequency of the bands as being due to support perturbation of the CO modes by the presence of oxide-bound species derived from  $\text{H}_2\text{CO}$ .<sup>22</sup> It is possible that the Rh gem dicarbonyl species produced from  $\text{H}_2\text{CO}$  also involved metallic rhodium rather than the usual  $\text{Rh}^+$ .

Finally, a study of acetone decomposition over 2.2% Rh/TiO<sub>2</sub> and 2.2% Rh/Al<sub>2</sub>O<sub>3</sub> was also performed here. However, the results were not inspiring. The infrared bands for gas-phase acetone disappeared, and GC indicated complete decomposition, upon heating at 440 K, but no adsorbed CO species or any other products could be detected by infrared. It would thus appear that acetone decomposes to inactive carbon over supported rhodium.

## Conclusions

From this study it may be concluded that: (1) methanol decomposes over supported Rh at 440 K to produce methane if  $\text{TiO}_2$  is the support or dimethyl ether if  $\text{Al}_2\text{O}_3$  is the support; (2) acetaldehyde decomposes over supported Rh at 440 K to produce methane and acetone; (3) acetone decomposes over supported Rh at 440 K to produce inactive carbon only; (4) potassium ions poison the formation of all products by presumably causing the production of large amounts of inactive carbon on the surface; and (5) the new Rh gem dicarbonyl state produced during the decomposition of acetaldehyde over 2.2% Rh/ $\text{Al}_2\text{O}_3$  probably refers to metallic rhodium rather than the usual  $\text{Rh}^+$  species.

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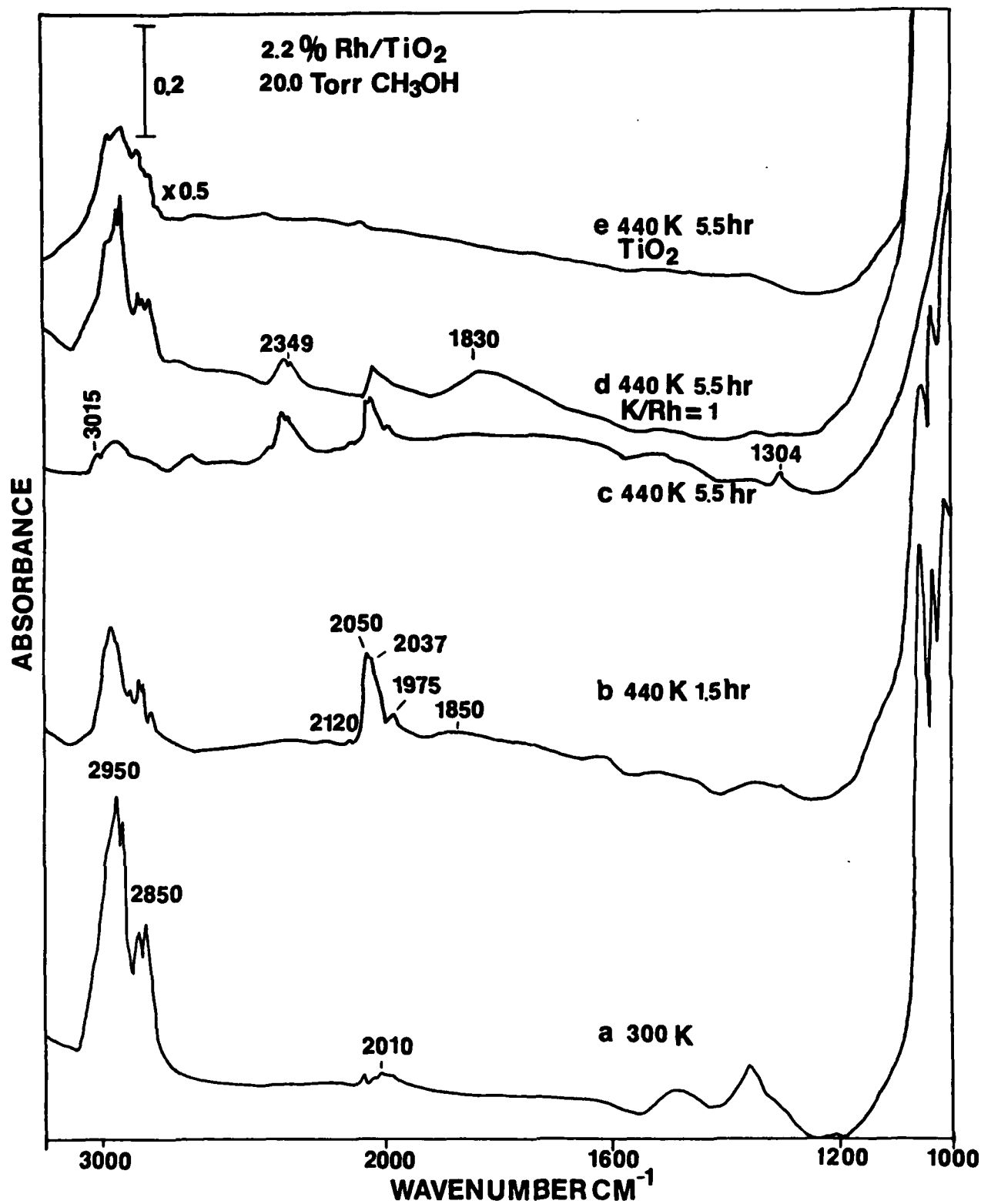
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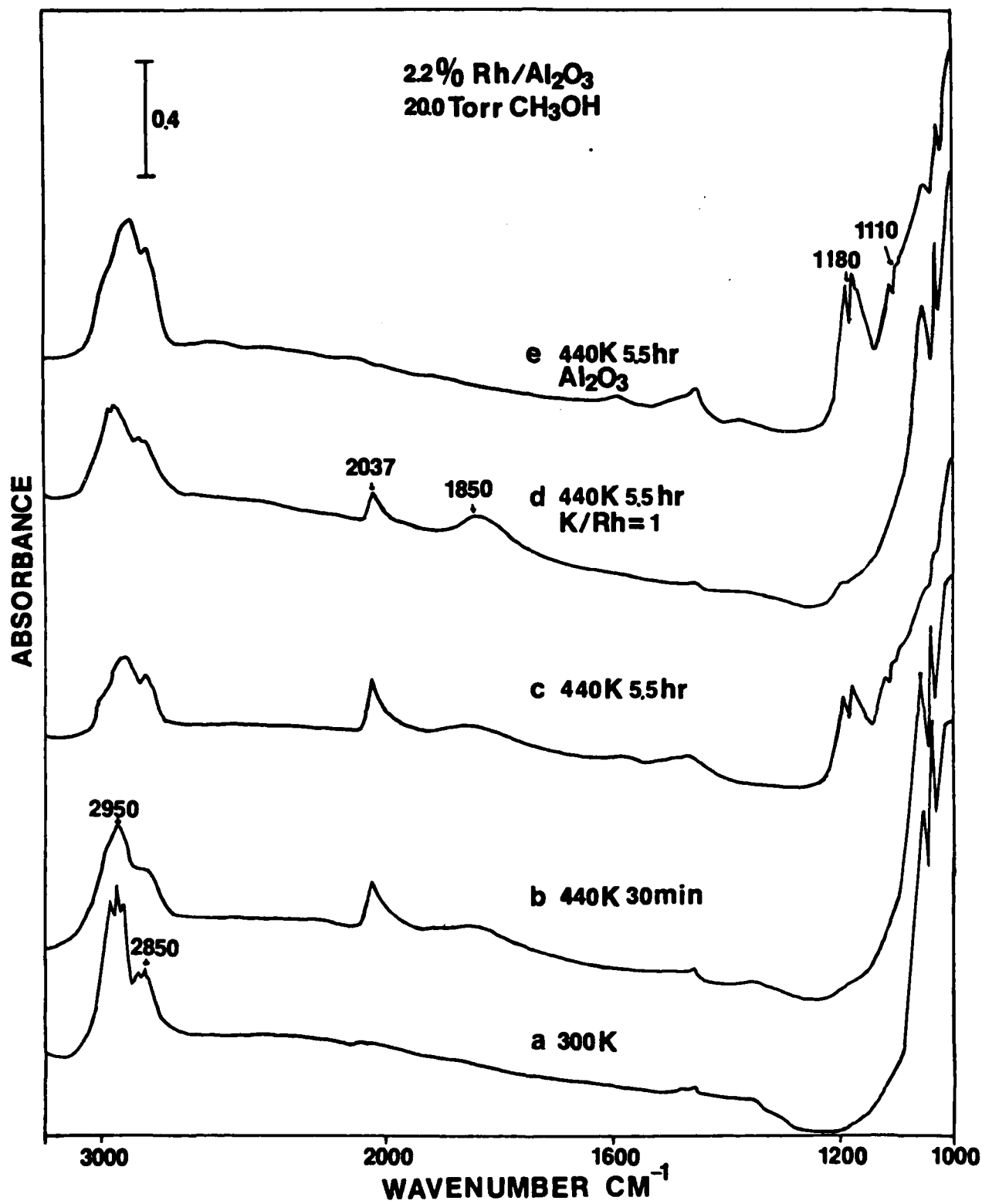
**Figure 1.** Infrared spectra for the decomposition of 20.0 Torr methanol over: (a, b, c) a 2.2% Rh/TiO<sub>2</sub> film (4.3 mg cm<sup>-2</sup>); (d) a 2.2% Rh/TiO<sub>2</sub> film containing K<sup>+</sup>; (e) a TiO<sub>2</sub> film.

**Figure 2.** Infrared spectra for the decomposition of 20.0 Torr methanol over: (a, b, c) a 2.2% Rh/Al<sub>2</sub>O<sub>3</sub> film (4.3 mg cm<sup>-2</sup>); (d) a 2.2% Rh/Al<sub>2</sub>O<sub>3</sub> film containing K<sup>+</sup>; (e) an Al<sub>2</sub>O<sub>3</sub> film.

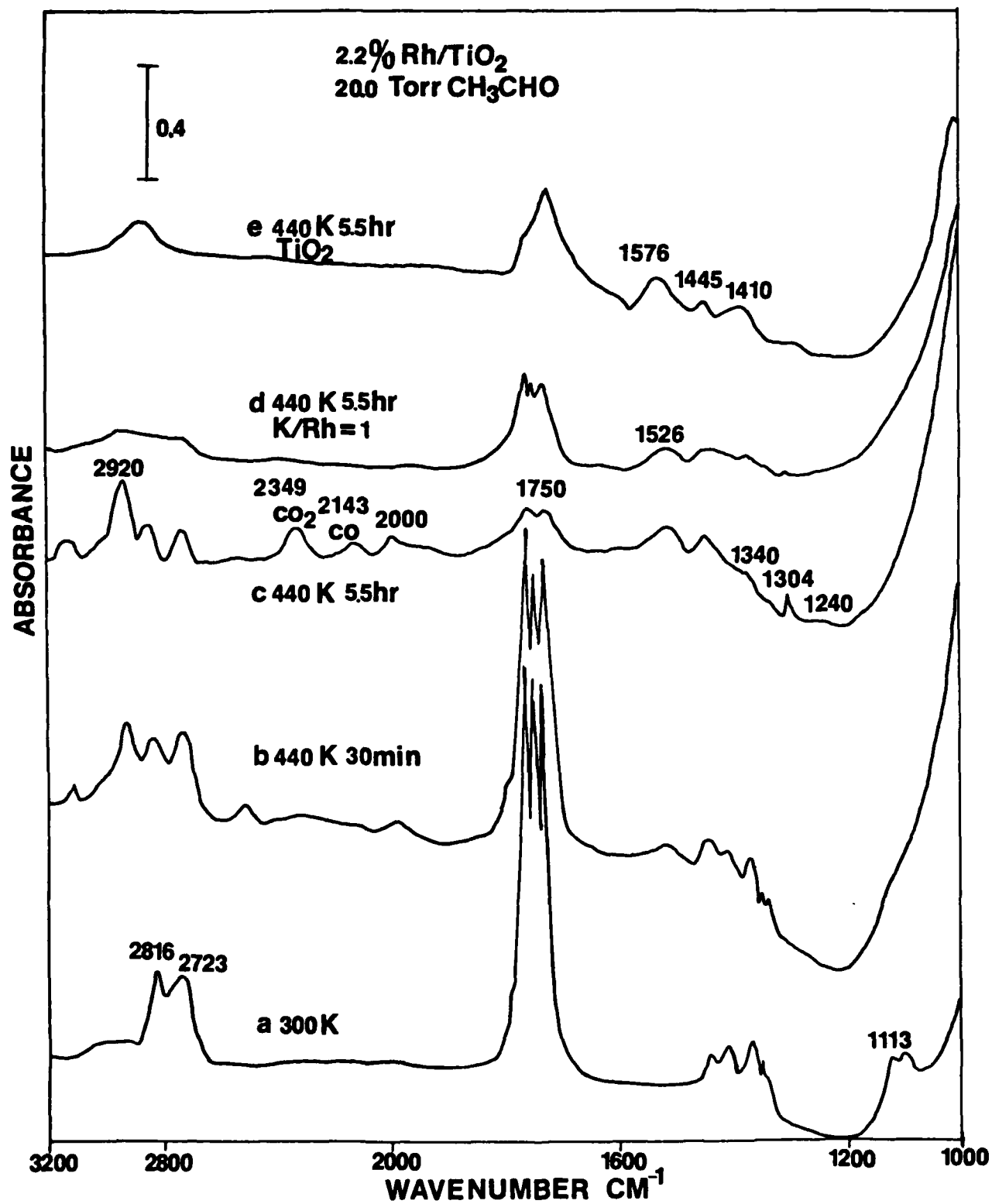
**Figure 3.** Infrared spectra for the decomposition of 20.0 Torr acetaldehyde over: (a, b, c) a 2.2% Rh/TiO<sub>2</sub> film (4.3 mg cm<sup>-2</sup>); (d) a 2.2% Rh/TiO<sub>2</sub> film containing K<sup>+</sup>; (e) a TiO<sub>2</sub> film.

**Figure 4.** Infrared spectra for the decomposition of 20.0 Torr acetaldehyde over: (a, b, c) a 2.2% Rh/Al<sub>2</sub>O<sub>3</sub> film (4.3 mg cm<sup>-2</sup>); (d) a 2.2% Rh/Al<sub>2</sub>O<sub>3</sub> film containing K<sup>+</sup>; (e) an Al<sub>2</sub>O<sub>3</sub> film.

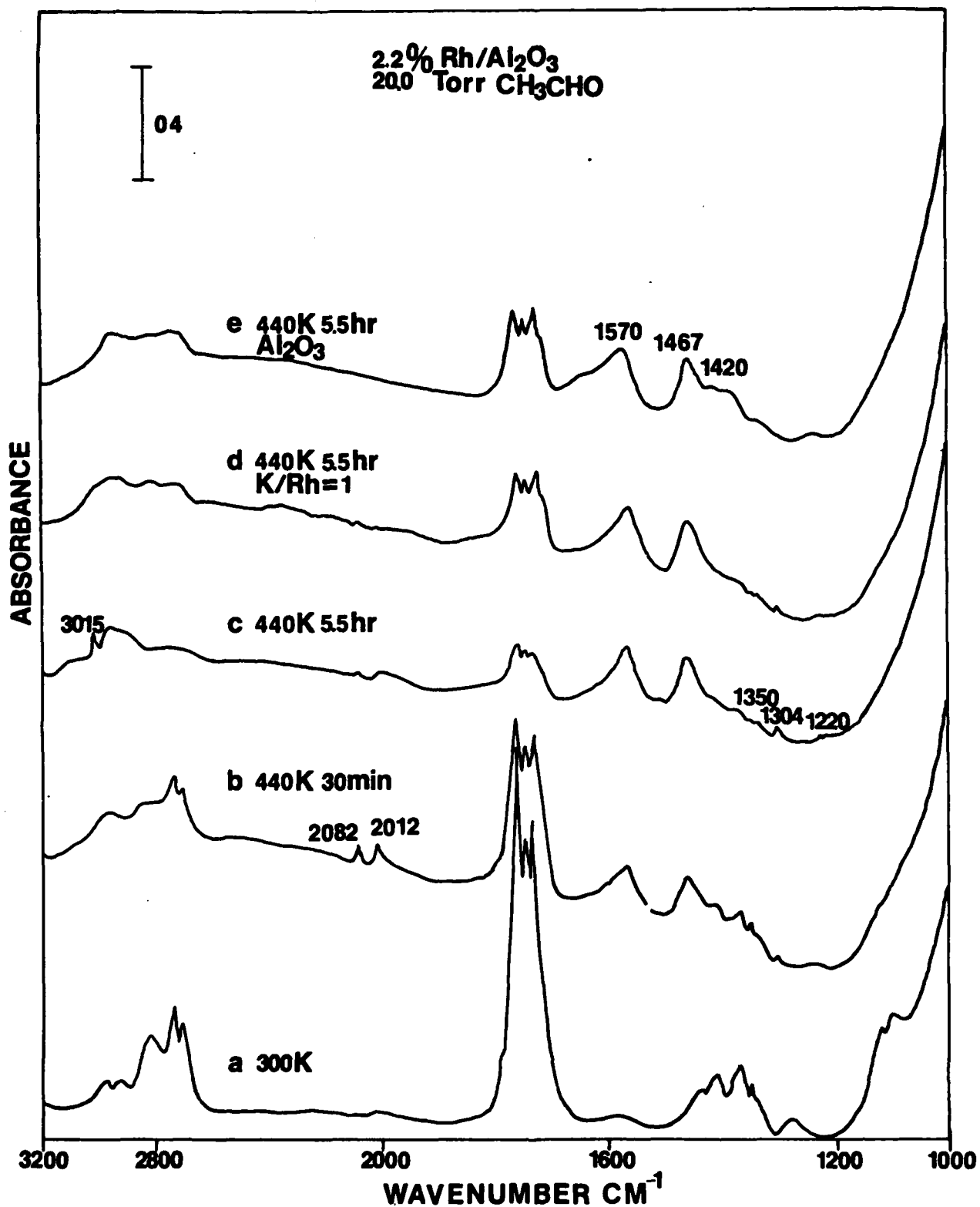




Worley & Doherty  
Fig. 2



Wiley: J. Catal.  
Fig. 3



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Department of Chemistry  
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

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Department of Chemistry  
Queen's University  
Kingston, Canada  
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Department of Chemistry  
Boston University  
685 Commonwealth Avenue  
Boston, Massachusetts 02215

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Department of Chemistry  
University of Rochester  
Rochester, New York 14627

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Department of Chemistry  
Harvard University  
Cambridge, Massachusetts 02138

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~~Auburn University~~  
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Dr. L. Vaska  
Department of Chemistry  
Clarkson College  
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