JOURNAL OF CATALYSIS **134**, 378–381 (1992)

Infrared Spectroscopy at High Pressure: Interaction of CO with Oxidized Rh/Al_2O_3

Infrared spectroscopy was used to study the interaction of CO with preoxidized Rh/Al_2O_3 catalyst films in a high-pressure cell reactor. An infrared band near 2125 cm^{-1}, which had previously been assigned to a $Rh^{2+}CO$ species and to one band component of an asymmetric $Rh(CO)_3$ species by two different laboratories, is now assigned to $Rh^{2+}CO$. This work demonstrates that gas-phase contributions from infrared-active species with high extinction coefficients can be eliminated from surface contributions, even at high pressures of the gas.

Since the pioneering work of Yang and Garland concerning infrared studies of the interaction of CO with Rh/Al_2O_3 (*1*), numerous investigations of this intriguing catalytic system have been reported (*2*). In fact, the interest in infrared studies of CO interactions with and reactions over supported rhodium apparently is still high, given the many reports which have appeared during the recent past (*3*–*9*). Although the $CO/Rh/Al_2O_3$ system has been thoroughly investigated using infrared spectroscopy, practically all of the work has concerned low pressures of CO (less than 100 Torr) and samples which were prereduced by exposure to H_2. This paper will report the results of recent studies using high pressures of CO and O_2 to interact with oxidized Rh/Al_2O_3 films.

The high-pressure-infrared-cell-reactor used in this study, which is capable of operation in the pressure and temperature ranges of 10^{-6} to 10^4 Torr and 100 to 600 K, respectively, has been described in detail previously (*10*). Films of Rh/Al_2O_3 were prepared by spraying a slurry of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey), Al_2O_3 (Aluminumoxid C from Degussa, 100 m^2g^{-1}), spectroscopic grade acetone, and distilled, deionized water onto a 25-mm CaF_2 infrared window held at 353 K. The solvents evaporated rapidly, leaving a thin film of $RhCl_3 \cdot 3H_2O/Al_2O_3$ (4.4 mg cm^{-2}) containing 2.2% by weight of Rh firmly attached to the window. The sample window was mounted into the cell reactor and subjected to pretreatment procedures which included evacuation at 10^{-6} torr for 1 h at 373 K, reduction with 100 Torr of H_2 (Air Products 99.999%, additional trapping at 77 K) in exposure/evacuation cycles of 10, 5, 10, and 20 min at 473 K, and then evacuation to 10^{-6} Torr for 1 h at 298 K. The sample was then exposed to CO (Mattheson 99.99%, trapped at 77 K) and/or O_2 (Air Products 99.993%, trapped at 158 K).

For those experiments involving high-pressure CO, half of the sample window was sprayed with $RhCl_3 \cdot 3H_2O/Al_2O_3$ and the other half with Al_2O_3 alone at the same film density using a masking technique similar to that described previously by Yates and coworkers (*4*). By translating the cell-reactor in the infrared beam path, we were able to subtract out the CO gas-phase infrared band contribution so that the surface species bands were not obscured. This technique worked admirably at pressures up to *ca.* 2000 Torr; above this pressure a residual CO gas-phase band at 2143 cm^{-1} began to appear even after attempted subtraction. It should be noted that this subtractive method also allows spectroscopic observation and compensation for any chemistry occurring on the Al_2O_3 support under conditions identical to those employed for the Rh/Al_2O_3 catalyst film (*4*).

All IR spectra were obtained with an IBM 32 Fourier transform spectrometer operated at 2 cm^{-1} resolution. Generally 500 scans

0021-9517/92 $3.00

were generated for each spectrum over a period of 7.5 min. The data displayed in this work represent difference spectra relative to appropriate reference spectra.

Yates and co-workers observed that isotopic exchange of ^{13}CO (g) with the gem dicarbonyl species on Rh/Al_2O_3 was rapid compared to desorption at 200 K (*11*). They postulated that a rhodium (I) tricarbonyl species could be involved in the isotopic exchange process (*12*) and attempted to observe such a tricarbonyl species spectroscopically for Rh/Al_2O_3 at low temperatures and relatively high CO pressures (*13*). They found that when the Rh/Al_2O_3 catalyst was preoxidized to produce primarily the gem dicarbonyl species, and then exposed to CO (g) at 241 K and pressures up to 423 Torr, infrared band components at 2120, 2078, and 2026 cm^{-1} could be deconvoluted using subtractive techniques. Earlier infrared work in these laboratories (*2*) had also detected a 2120 cm^{-1} band for CO adsorbed on preoxidized Rh/Al_2O_3 in addition to the usual two bands for the gem dicarbonyl species. We assigned the 2120 cm^{-1} band to a $Rh^{2+}CO$ species (probably a carbonyl oxide). Our basis for this assignment was that an unreduced $RhCl_3 \cdot 3H_2O/Al_2O_3$ sample exposed to CO at 298 K produced a carbonyl species giving an infrared band at 2136 cm^{-1} which logically could be assigned to $Rh^{+3}CO$ created through ligand exchange. It is widely accepted that the 2100 and 2030 cm^{-1} band components refer to $Rh^{1+}(CO)_2$. Thus, it seemed logical to assign the 2120 cm^{-1} band to a species having its rhodium oxidation state intermediate between $+3$ and $+1$, i.e., $+2$. However, the work of Wang and Yates questioned this assignment; they suggested that the three band components under high-pressure and low-temperature conditions referred to a $Rh^{+}(CO)_3$ species with symmetry lower than C_{3v} (*13*). It should be noted that recent infrared work by Bell and co-workers was suggestive of a $Ru(CO)_3$ species for Ru/SiO_2 also (*14*), so tricarbonyl surface species are obviously a topic of interest in catalysis.

In this work a preoxidized 2.2% Rh/Al_2O_3 film was exposed to increasing pressures of CO at 298 K. Preoxidation consisted of exposure of a prereduced sample to 2012 Torr of O_2 at 298 K for 36 h. As the pressure of CO was increased over the surface, the gem dicarbonyl species developed as evidenced by infrared bands at 2022 and 2097 cm^{-1}. A small band near 2122 cm^{-1} also developed until the CO pressure reached 40 Torr and then was unchanged in intensity at 110 and 517 Torr. Little or no band development occurred in the 2050 or 1900 cm^{-1} regions, suggestive of linear or bridged carbonyl metallic Rh sites. The fact that the 2122 cm^{-1} band did not continue to increase in intensity concomitantly with the gem dicarbonyl bands renders the assignments of these three bands to a tricarbonyl species unlikely. The split sample and subtractive techniques were effective in eliminating the gas-phase CO contribution to the infrared spectrum, which would normally be very large at 517 Torr.

Figure 1 indicates the changes in the infrared spectrum for the same sample as the temperature was increased in the >500 Torr CO atmosphere. The gem dicarbonyl species bands increased in intensity with heating up to 399 K (Fig. 1(a)–(c)) and then decreased slightly indicating desorption or decomposition of this species at 423 K (Fig. 1(d)). At 298 K, following the heating experiments (Fig. 1(e)), the gem dicarbonyl species bands had declined in intensity by ca. 50% while weak, broad bands characteristic of the linear and bridged species developed at 2070 and 1850–1900 cm^{-1}, respectively. The band at 2122 cm^{-1} began to decline markedly in intensity at 399 K (Fig. 1(c), left inset) and disappeared completely by the end of the experiment. These results again must argue against the presence of a $Rh(CO)_3$ species; rather we believe that the 2122 cm^{-1} band should be assigned to a Rh^{2+} species as we suggested earlier (*2*). It is clear that CO(g) served as a reducing agent in this experiment, for the Rh^{2+} and Rh^{1+} surface carbonyls were diminished as the metallic carbonyl species formed.

In a second series of experiments high

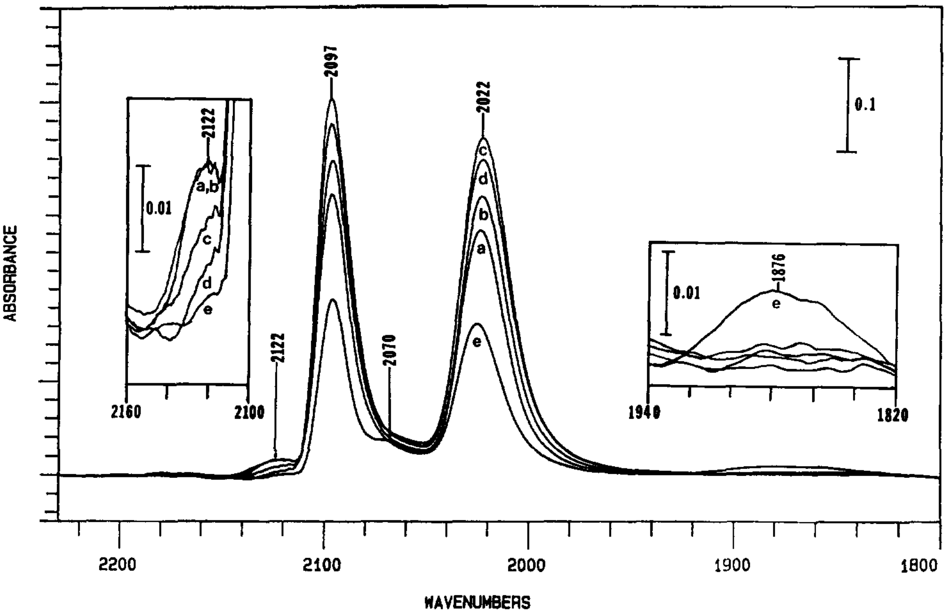

FIG. 1. Infrared spectra for a preoxidized (2012 Torr O_2 for 36 h at 298 K) 2.2% Rh/Al_2O_3 film (4.4 mg cm^{-2}) under the conditions: (a) 517 Torr CO for 5 min at 298 K, (b) 536 Torr CO for 15 min at 362 K, (c) 547 Torr CO for 20 min at 399 K, (d) 554 Torr CO for 15 min at 423 K, (e) 523 Torr CO for 15 min at 298 K.

pressure O_2 was added to the cell reactor which contained a prereduced 2.2% Rh/Al_2O_3 film which had been exposed to a low pressure of CO(g). The infrared spectrum of the surface following exposure to 0.5 Torr of CO and evacuation contained the usual gem dicarbonyl, linear, and bridged species bands. Following exposure of this surface to CO, the sample was dosed with 134 Torr O_2 for 13 min at 298 K, resulting in the reduction of intensity of the linear RhCO species band near 2050 cm^{-1}, and vanishing of the bridged Rh_2CO species band at 1850 cm^{-1}. These observations are in accord with previous results obtained by Kiss and Gonzalez (*15*). A small band at ca. 2125 cm^{-1} indicated the formation of some $Rh^{2+}CO$ species; this band, as well as one growing in at 2350 cm^{-1} for CO_2(g), is indicative of surface oxidation. The $Rh^{1+}(CO)_2$ bands also diminished somewhat upon oxidation. As higher pressures of O_2 (up to 8040 Torr) were employed at 298 K, the observations noted above were accentuated.

Figure 2 shows the infrared spectra which result upon heating the sample in the presence of 8040–8998 Torr of O_2. All of the surface CO species diminish upon heating with concomitant production of CO_2(g). At 455 K and 8998 Torr O_2 the only surface species which remained (Fig. 2(e)) was the $Rh^{2+}CO$ species giving rise to the 2125 cm^{-1} band. This band, which then remains unchanged upon cooling to 298 K, cannot be a third component for a $Rh(CO)_3$ species, because it neither grows or diminishes in a regular pattern with the 2101 and 2031 cm^{-1} bands.

Even though we are confident that the 2122–2125 cm^{-1} band observed in this study should be assigned to a $Rh^{2+}CO$ species, it is conceivable that the three band components for a tricarbonyl species as reported by Wang and Yates (*13*) are nearly coincidental in frequency with the $Rh^{2+}CO$ and gem dicarbonyl bands (*16*). The conditions under which the two studies were conducted were not the same.

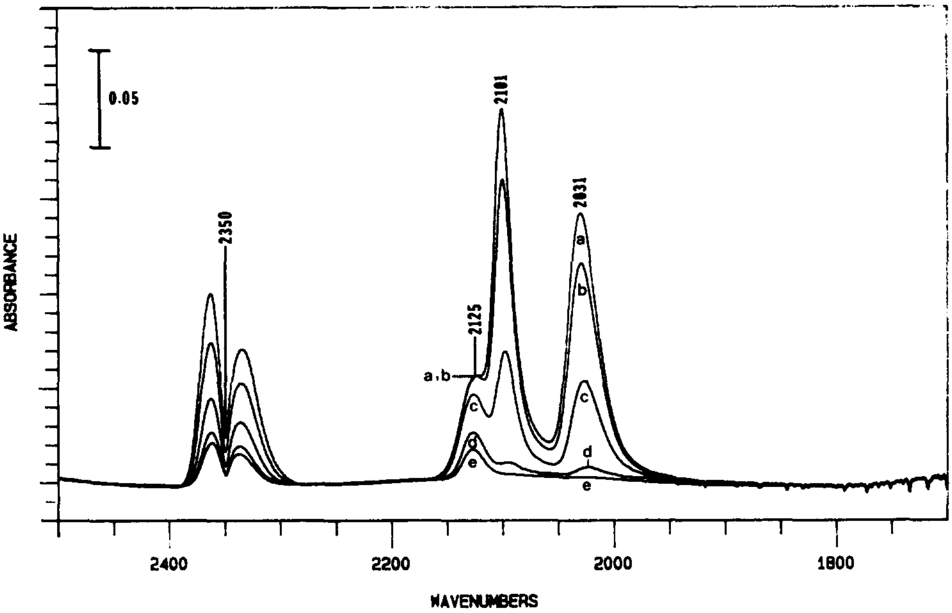

FIG. 2. Infrared spectra for a prereduced (see description of experimental procedure) 2.2% Rh/Al_2O_3 film (4.4 mg cm^{-2}) exposed at 298 K to 0.5 Torr CO for 5 min at 298 K followed by evacuation, and then to (a) 8040 Torr O_2 for 13 h at 298 K, (b) 8245 Torr O_2 for 45 min at 332 K, (c) 8530 Torr O_2 for 45 min at 378 K, (d) 8833 Torr O_2 for 45 min at 427 K, (e) 8998 Torr O_2 for 25 min at 455 K.

ACKNOWLEDGMENTS

This work was supported in part by the Innovative Science and Technology Office of the Strategic Defense Initiative through the Naval Surface Warfare Center, Contract N60921-91-C-0078.

REFERENCES

1. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61,** 1504 (1957).
2. For a review of the historical development of this topic, see Rice, C. A., Worley, S. D., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **74,** 6487 (1981).
3. Solymosi, F., and Knözinger, H., *J. Chem. Soc. Faraday Trans.* **86,** 389 (1990).
4. Basu, P., Panaytov, D., and Yates, J. T., *J. Am. Chem. Soc.* **110,** 2074 (1988).
5. Buchanan, D. A., Hernandez, M. E., Solymosi, F., and White, J. M., *J. Catal.* **125,** 456 (1990).
6. Paul, D. K., and Yates, J. T., *J. Phys. Chem.* **95,** 1699 (1991).
7. Zaki, M. I. Ballinger, T. H., and Yates, J. T., *J. Phys. Chem.* **95,** 4028 (1991).
8. Lu, G., Darwell, J. E., and Crowell, J. E., *J. Phys. Chem.* **94,** 8326 (1990).
9. Anderson, J. A., and Rochester, C. H., *J. Chem. Soc. Faraday Trans.* **87,** 1479 (1991).
10. Wey, J. P., Burkett, H. D., Neely, W. C., and Worley, S. D., *J. Am. Chem. Soc.* **113,** 2919 (1991).
11. Yates, J. T., Duncan, T. M., Worley, S. D., and Vaughan, R. W., *J. Chem. Phys.* **70,** 1219 (1979).
12. Yates, J. T., Duncan, T. M., and Vaughan, R. W., *J. Chem. Phys.* **71,** 3908 (1979).
13. Wang, H. P., and Yates, J. T., *J. Catal.* **89,** 79 (1984).
14. Yokomizo, G. H., Louis, C., and Bell, A. T., *J. Catal.* **120,** 1 (1989).
15. Kiss, J. T., and Gonzalez, R. D., *J. Phys. Chem.* **88,** 898 (1984).
16. We thank a referee for this suggestion.

J. P. WEY
W. C. NEELY
S. D. WORLEY[1]

Department of Chemistry
Auburn University
Auburn, Alabama 36849

Received June 25, 1991

---

[1] To whom correspondence should be addressed.