$$F_4(\alpha,\beta,\gamma) = \cos^2\alpha + \sin^2\alpha = 1$$

$$F_5(\alpha,\beta,\gamma) = \cos^2\beta + \sin^2\beta = 1$$

$$F_6(\alpha,\beta,\gamma) = \cos^2\gamma + \sin^2\gamma = 1$$

we obtain a system of six simultaneous equations in six unknowns that can be treated as independent and are collected in a vector $\mathbf{q} \equiv \{q_m\} \equiv \{\cos\alpha, \sin\alpha, \cos\beta, \sin\beta, \cos\gamma, \sin\gamma\}$:

$$F_n(\mathbf{q}) = H_n,\ n = 1\text{–}6$$

This equation set is solved iteratively. First, we choose an initial guess $\mathbf{q}^{(0)}$ and evaluate $h_n = F_n(\mathbf{q}^{(0)})$. From the partial derivatives of the functions of F_n with respect to the unknowns collected in $\mathbf{q}$, we have

$$\Delta F_n = \sum_m \Delta q_m(\partial F_n/\partial q_m)$$

as the linear approximation to the changes in the values of F_n that will be caused by a change $\Delta\mathbf{q}$ in the unknowns. To reach the solution, we would require $\Delta F_n = H_n - h_n$, $n = 1$–6. These six linear equations are solved for the Δq_m's. Since the functions F_n are not linear in q_m, it is necessary to take $\mathbf{q}^{(1)} = \mathbf{q}^{(0)} + \Delta\mathbf{q}$ and iterate. In practice, damping is usually required so that we actually set $\Delta F_n = (H_n - h_n)t$ for a suitably chosen $0 < t \ll 1$. Note that if the summation over m contained only one term, $m = 1$, and if there were only one function F_n, $n = 1$, then this iterative procedure would be exactly the Newton–Raphson method.

Registry No. *s-trans*-1,3-Butadiene, 106-99-0.

Infrared Spectroscopy at High Pressure. Interaction of N_2 with Rh/Al_2O_3 at Ambient Temperature

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Abstract: The design and construction of a new high-pressure infrared-cell reactor capable of variable-temperature operation which should be useful in the study of a variety of chemical reactions has been described. The cell reactor has been employed in this work to investigate the interaction of N_2 with Rh/Al_2O_3 catalyst films in the pressure regime 1×10^{-6} to 9000 Torr at 298 K. The results obtained were in good accord with those obtained by Wang and Yates for similar catalysts at low temperatures and pressures. Infrared bands for chemisorbed and physisorbed N_2 species have been detected and tentatively assigned.

I. Introduction

For the past decade work in these laboratories has focused on the use of transmission infrared spectroscopy to study the interaction of small molecules with supported transition-metal films, such as $CO/Rh/X$ ($X = Al_2O_3$, SiO_2, and TiO_2).[1] In particular studies of "simple" reactions such as the hydrogenation of CO[2] and CO_2[3] or the CO/NH_3 system[4] have provided intriguing information concerning the structures of intermediate species adsorbed on the supported catalyst films. Most of the prior work pertained to the reactions at sub-atmospheric pressure conditions, typically less than 100 Torr.[1-4] However, recent work here concerning the reaction of CO and CO_2 with H_2 over Pd/La_2O_3 films at high pressure (8000 Torr) to produce selectively methanol has led us to the conclusion that Fourier transform infrared spectroscopy can be employed to obtain useful information about reactions normally performed at several atmospheres of pressure.[5]

This paper will discuss the performance of a newly designed high-pressure infrared-cell reactor. The initial results obtained with the reactor, which will be addressed here, concerned the reaction of N_2 with Rh/Al_2O_3 films at 298 K as a function of pressure. While N_2 will interact with supported Rh catalysts at ambient temperatures or above if the support is TiO_2 or SiO_2 or if potassium promotion of Rh/Al_2O_3 is employed,[6-11] prior work on the unpromoted $N_2/Rh/Al_2O_3$ system has been confined to low-temperature studies because of the very weak interaction at ambient temperatures.[12] Indeed, the elegant investigation of Wang and Yates has demonstrated the considerable versatility of low-temperature infrared spectroscopy for studying the weak interaction of N_2 with Rh/Al_2O_3.[12] This paper will discuss the similarities and differences between the low-temperature, low-pressure work[12] and the current ambient-temperature, high-pressure studies.

II. Experimental Section

Schematic diagrams of the new high-pressure infrared-cell reactor used in this study are shown in Figures 1 and 2. The reactor was fabricated from three 4.62-in. stainless steel conflat flanges which were bolted together. The outer two flanges each contained 13-mm CaF_2 infrared windows held in place by 0.375-in. ultra-torr adaptor fittings. This arrangement allowed a base vacuum in the cell of ca. 1×10^{-8} Torr, as well as operating pressures of at least 13 atm. Both outer window assemblies could be cooled by flowing water. One of the outer flanges also contained ports for attachment to the vacuum and high-pressure manifolds and for gas chromatographic analysis. The middle flange

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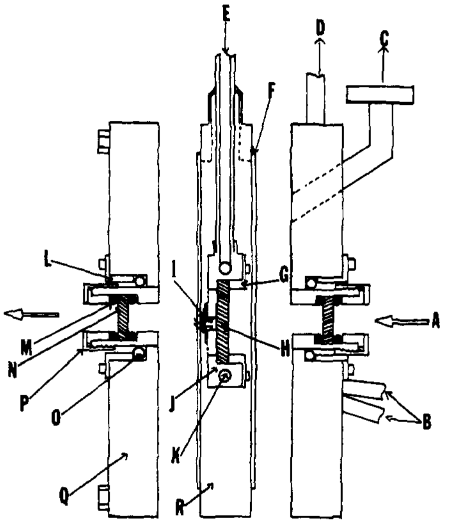
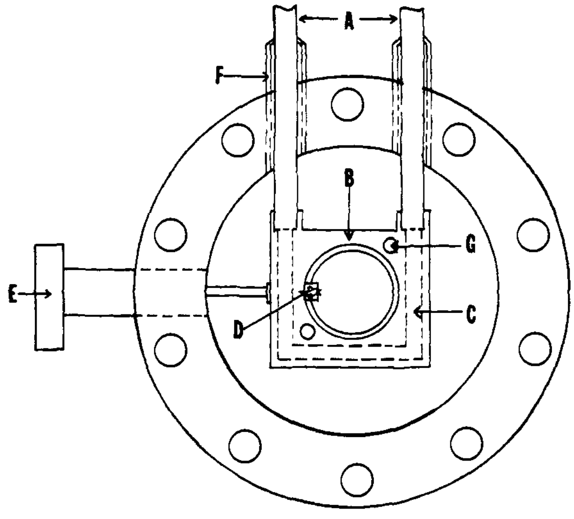


A: IR Beam B: Gas Inlet and Outlet C: To Vacuum D: To GC E: Heating/Cooling Gas Inlet F: Copper Gasket G: Aluminum Sample Holder Ring H: CaF_2 Sample Window I: Cr-Al Thermocouple and Cap J: Stainless Steel Sample Holder Cap K: U-Shaped Heating/Cooling Tunnel L: Aluminum Cap M: 13mm Viton O-ring N: 13mm CaF_2 Window O: Water Cooling Copper Tubing P: 0.375 in Ultra-Torr Cap Q: 4.62 in Stainless Steel Flange R: 4.62 in Stainless Steel Double-Sided Conflat Flange

Figure 1. Side view of the high-pressure infrared-cell reactor used in this study.



A: Heating/Cooling Gas Inlet/Outlet B: Stainless Steel Sample Holder Block C: Heating/Cooling Gas U-shaped Tunnel D: Cr-Al Thermocouple E: 1.33 in Thermocouple Feedthrough Flange F: 0.5 in Stainless Steel Tubing G: Sample Holder Ring Mounting Screw

Figure 2. End view of the sample compartment of the high-pressure infrared-cell reactor.

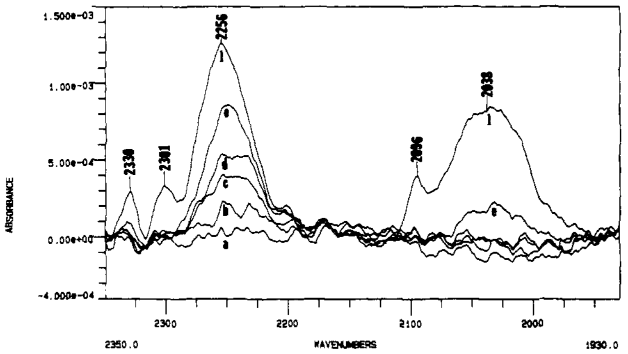


Figure 3. Infrared spectra for N_2 and impurity CO adsorbed on a 2.2% Rh/Al_2O_3 film at 298 K after reduction: (a) 30, (b) 244, (c) 1210, (d) 2006, (e) 4013, and (f) 8000 Torr of N_2.

shown in Figure 2 contained a stainless steel block (0.43 in. thick) in which a U-shaped tunnel (0.152-in. diameter) was drilled for use in heating and cooling the samples by passage of externally heated or cooled nitrogen gas through insulated 0.25-in. stainless steel tubing. This arrangement prevented the introduction of impurities from internal heating wire or refractory cements. A third CaF_2 infrared window (25 mm diameter, 2 mm thick) containing the catalyst *film* was *mounted in* the center of the heating/cooling block by means of a small recessed lip and a thin aluminum ring held in place by two small mounting screws. A small well under the edge of the sample window contained a chromel-alumel thermocouple used to monitor the temperature of the film; the thermocouple leads exited through electrical feed-throughs. The gas path length in the cell exposed to the infrared/beam was ca. 33 mm.

The external vacuum and gas-handling manifold was also constructed of stainless steel and connected to a cryopump and a 60 L s^{-1} ion pump. Pressure measurements were made with an MKS Baratron capacitance manometer operable up to 10000 Torr. Temperature control was effected by passing nitrogen through an 18-in. Pyrex tube containing coiled nichrome wire for controlled resisitive heating. We have operated the cell at temperatures as high as 600 K and as low as 110 K using cold flowing N_2. All spectra were obtained with an IBM 32 Fourier transform spectrometer operated at 2-cm^{-1} resolution. Generally 500 scans were generated for each spectrum over a period of 7.5 min. All IR data displayed in this work represent difference spectra relative to appropriate reference spectra.

Sample films were prepared with techniques employed here previously.[1-5] Briefly, a slurry containing $RhCl_3{\cdot}3H_2O$ (Johnson Matthey), alumina (Aluminumoxid C from Degussa, 100 m^2 g^{-1}), spectroscopic grade acetone, and distilled, deionized water was sprayed onto the 25-mm CaF_2 window held at 80 °C. The solvents evaporated rapidly leaving a thin film of $RhCl_3{\cdot}3H_2O/Al_2O_3$ (4.4 mg cm^{-2}) at either 2.2 or 0.5% by weight Rh attached to the window. The sample window was mounted in the cell reactor, and the sample was maintained at 373 K at 10^{-6} Torr for 1 h. Then reduction was accomplished with 100 Torr of H_2 (Air Products 99.999%, additional purification at 77 K) and evacuation cycles of 10, 5, 10, and 20 min at 473 K. After being cooled, the sample was held at 10^{-6} Torr for 1 h and then exposed to successively higher pressures of N_2 (Air Products 99.999%, trapped at 77 K at low pressure and 158 K at high pressure) at ambient temperature (ca. 298 K). Following the exposure to N_2, the sample was evacuated, reduced again with 100 Torr of H_2 for two 10-min cycles at 473 K, and then exposed to 100 Torr of O_2 (Air Products 99.993%, trapped at 77 K) for 5 min at 298 K. After evacuation for 1 h at 10^{-6} Torr, the oxidized sample was exposed to successively higher pressures of N_2. In one experiment CO (Matheson 99.99%) was introduced into the cell reactor following normal reduction. In this case 50 Torr of CO was exposed to a 0.5% Rh/Al_2O_3 sample for 5 min to saturate the surface, followed by heating at 403 K for 2.5 h at 10^{-6} Torr. Upon cooling this sample, the surface was found by infrared analysis to contain almost only the well-known Rh gem dicarbonyl species.[1]

III. Results and Discussion

Infrared spectra corresponding to a reduced 2.2% Rh/Al_2O_3 catalyst film exposed to N_2 in the pressure range of 30–8000 Torr at 298 K are shown in Figure 3. The lowest pressure at which a band for a chemisorbed N_2 species was discernible was 244 Torr (Figure 3b). This band near 2250 cm^{-1}, which may contain two or more components corresponding to multiple surface species, intensified and shifted to higher wavenumber as the pressure was increased. The band at 2256 cm^{-1} at 8000 Torr of pressure resembles closely the one observed by Wang and Yates[12] in their low-temperature work (90–189 K) for a 2.2% Rh/Al_2O_3 catalyst at pressures up to 218 Torr. At the highest pressure studied (8000 Torr) two additional N_2 bands were resolved at 2330 and 2301 cm^{-1}. Wang and Yates also observed a band at 2331 cm^{-1} for a reduced 2.2% Rh/Al_2O_3 surface as well as for an Al_2O_3 surface alone which declined in intensity with increasing temperature, disappearing completely at 189 K, which they assigned to a physisorbed N_2 species on the Al_2O_3 support.[12] It is interesting that this physisorbed N_2 can exist on the Al_2O_3 even at ambient temperature when 4000–8000 Torr of gas-phase N_2 is present.

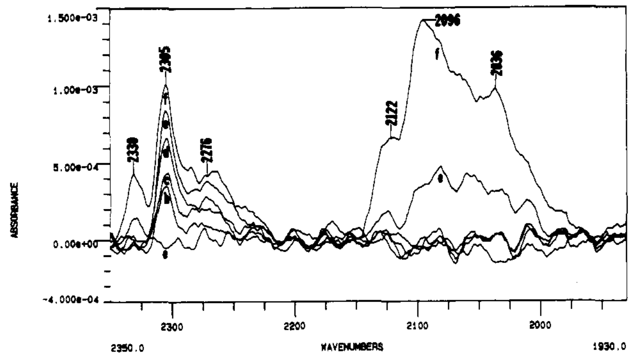


Figure 4. Infrared spectra for N_2 and impurity CO adsorbed on a 2.2% Rh/Al_2O_3 film at 298 K after oxidation: (a) 1×10^{-6}, (b) 50, (c) 202, (d) 790, (e) 3890, and (f) 8000 Torr of N_2.

The band which we observe at 2301 cm^{-1} (Figure 3f) was not observed at low temperature for a reduced catalyst, but rather was detected at 2303 cm^{-1} even at temperatures in the 200–300 K range for a Rh/Al_2O_3 catalyst oxidized at 309 K.[12] Wang and Yates assigned this band to an oxidized RhN_2 species and concluded that the 2257-cm^{-1} band referred to chemisorbed N_2 on a metallic Rh site, rather than a Rh^+ site. The spectra in Figure 3a–d corresponding to N_2 pressures up to 2006 Torr show no structure in the 1800–2135-cm^{-1} region indicative of adsorbed RhCO species. However, when the pressure reached 4013 Torr, a weak, broad band near 2040 cm^{-1} appeared (Figure 3e). This band can be assigned to the well-known "linear" RhCO species which always appears on 2.2% Rh/Al_2O_3 surfaces at extremely low pressures of CO gas.[1] This species results from the small amount of CO impurity which was impossible to remove from the high-pressure stream of N_2. When the N_2 pressure was increased to 8000 Torr (Figure 3f), the spectral features corresponding to adsorbed CO species increased markedly in intensity, and, in fact, the "gem dicarbonyl" Rh species giving bands at 2096 cm^{-1} and ca. 2030 cm^{-1} was clearly present as well as the linear RhCO species (ca. 2050 cm^{-1}) and bridged Rh_2CO (broad band in the 1800–2000-cm^{-1} region not shown in Figure 3f). The intensities of the RhCO bands approach that of the RhN_2 band at 2256 cm^{-1} emphasizing the fact that CO binding to Rh is much stronger than that of N_2 to Rh for Rh/Al_2O_3 catalysts. Although generally the presence of impurity CO would be considered undesirable in a study such as this, in this case it fortuitously led to interesting results and conclusions. The RhN_2 band at 2301 cm^{-1} in Figure 3f can be directly attributed to the presence of impurity CO, because it has been well established that CO disrupts Rh metallic sites,[13] and it can cause partial oxidation of Rh to create highly dispersed Rh^+ sites[14] which are produced as isolated OH groups on Al_2O_3 are consumed.[15] Thus a $Rh^{\delta+}N_2$ species is clearly responsible for the band at 2301 cm^{-1} in accord with the observations of Wang and Yates.[12]

Upon evacuation at 298 K, all bands attributed here to N_2 surface species disappeared immediately indicating that the N_2 interaction with Rh/Al_2O_3 is certainly reversible. However, evacuation alone at 298 K did not affect the intensities of the tightly bound RhCO surface species bands. Studies on other samples treated in an analogous manner have shown that reexposure of the surface to N_2 gas at high pressure (8000 Torr) again causes the formation of the species giving rise to the 2256-cm^{-1} RhN_2 band, but upon each reexposure, the intensity of the band declines in concert with an increase in the intensity of the RhCO bands caused by additional impurity CO. Thus CO and N_2 seem to be occupying the same surface sites. The exception to this is the 2330-cm^{-1} band attributed to physisorbed N_2 on Al_2O_3 which appears at 8000 Torr even for surfaces saturated with adsorbed RhCO species. This observation, in fact, confirms the assignment[12] of the 2330-cm^{-1} band to physisorbed N_2 on Al_2O_3.

Table I. Infrared Frequencies and Assignments for RhN_2 Species Observed for 2.2% Rh/Al_2O_3 Catalysts

$\nu(N_2)$ (this work),[a] cm^{-1}	assignment[a]	$\nu(N_2)$ (ref 12),[b] cm^{-1}	assignment[b]
2330	N_2/Al_2O_3 physisorbed	2331	N_2/Al_2O_3 physisorbed
2301	$N_2/Rh^{\delta+}$	2303	$N_2/Rh^{\delta+}$
2276	$N_2/Rh^{\delta+}$	2270	$N_2/Rh^{\delta+}$
2256	N_2/Rh^0 or N_2Rh^+	2257	N_2/Rh^0

[a] 298 K, 8000 Torr of N_2. [b] Low temperatures, low pressures of N_2.

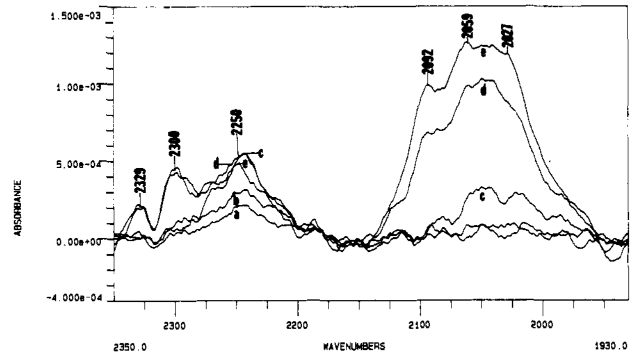


Figure 5. Infrared spectra for N_2 and impurity CO adsorbed on a 0.5% Rh/Al_2O_3 film at 298 K after reduction: (a) 404, (b) 790, (c) 2000, (d) 6083, and (e) 8007 Torr of N_2.

Following reduction of the sample discussed above at 473 K, which eliminated the RhCO surface species causing the spectral features in the 1800–2135-cm^{-1} region of Figure 3, the sample was exposed to O_2 at 298 K (see Experimental Section) and then to successively higher pressures of N_2. The results of this experiment are shown in Figure 4. As the N_2 pressure was increased from 0 to 790 Torr, infrared bands developed at 2276 and 2305 cm^{-1}. Wang and Yates reported similar bands at 2270 and 2303 cm^{-1} in their low-temperature studies of N_2 over a Rh/Al_2O_3 surface oxidized under similar conditions to those here.[12] These two bands may be assigned to $Rh^{\delta+}N_2$ species, the latter being observed as well on the reduced surface following oxidation of Rh^0 sites facilitated by the presence of CO (Figure 3f). When the pressure of N_2 was increased to 3890 Torr, impurity RhCO species began to appear, and at 8000 Torr spectral features (Figure 4f) due to the "gem dicarbonyl" Rh^+ species at 2036 and 2096 cm^{-1} and a $Rh^{2+}CO$ species (2120 cm^{-1})[1] were prominent. Also, at high pressure (3890–8000 Torr) an infrared band at 2330 cm^{-1} for physisorbed N_2 on Al_2O_3 developed. The fact that the physisorbed species band underwent almost no shift in wavenumber relative to a reduced surface indicates that any interaction of that species with $Rh^{\delta+}$ sites must be extremely weak. The 2256-cm^{-1} band observed for chemisorbed N_2 on reduced Rh/Al_2O_3 in Figure 3 is not present in Figure 4, although it is quite possible that the surface site responsible for this N_2 species has now been oxidized to the $Rh^{\delta+}$ site responsible for the 2276-cm^{-1} band in Figure 4. A summary of the various surface N_2 species found in this work and in the low-temperature, low-pressure work of Wang and Yates[12] is given in Table I.

Figure 5 shows the results of exposure of successively higher pressures of N_2 to a prereduced 0.5% Rh/Al_2O_3 catalyst film. Wang and Yates were not able to detect the chemisorbed N_2 on a 0.5% Rh/Al_2O_3 sample under their conditions of low pressure and temperature.[12] This observation led them to conclude that the 2256-cm^{-1} band refers to N_2 on metallic Rh sites;[12] it has been concluded previously that 0.5% Rh/Al_2O_3 catalysts are highly dispersed and in the presence of CO have only Rh^+ gem dicarbonyl surface sites.[1] However, by using the increased sensitivity provided by high-pressure and FTIR difference spectra capability, it is evident from Figure 5 that RhN_2 species can be detected at

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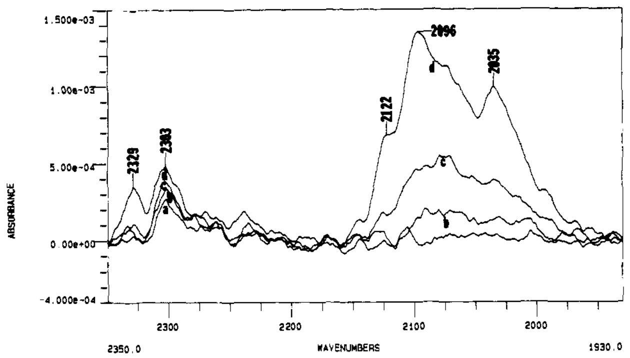

Figure 6. Infrared spectra for N_2 and impurity CO adsorbed on a 0.5% Rh/Al_2O_3 film at 298 K after oxidation: (a) 205, (b) 1720, (c) 3880, and (d) 9008 Torr of N_2.

ambient temperature and high pressure on a 0.5% Rh/Al_2O_3 surface. Again, a 2250-cm^{-1} band appears at lower pressure (Figure 5a,b) and grows in intensity until RhCO bands begin to dominate. When the RhCO surface species appear above 2000 Torr of N_2 pressure, the 2300-cm^{-1} band corresponding to a $Rh^{\delta+}N_2$ species again appears, and the physisorbed N_2 species (2329-cm^{-1} band) is again observed at high pressure. It is interesting that with the increased FTIR sensitivity now available in our laboratories small amounts of linear (2059 cm^{-1}) and bridged (1800–1900 cm^{-1}) RhCO species in addition to the usual gem dicarbonyl species (2092 and 2027 cm^{-1}) are now detected for the 0.5% Rh/Al_2O_3 catalyst film in contrast to early results with dispersive infrared.[1] It would appear that the RhN_2 species causing the band at 2250 cm^{-1} ceases to develop as the gem dicarbonyl bands intensify, as evidenced by a decline in intensity of the 2250-cm^{-1} band in the 6083–8007 Torr of N_2 pressure regime. This could possibly indicate that the RhN_2 species (absorbing at 2250 cm^{-1}) forms on partially reduced sites normally occupied by the Rh^+ gem dicarbonyl species, rather than on sites occupied by the linear metallic RhCO species, although the gem dicarbonyl bands are severely overlapped by an intensifying Rh^0CO band at 2059 cm^{-1}.

When the 0.5% Rh/Al_2O_3 sample was reduced again to rid the surface of adsorbed CO, and subsequently oxidized at 298 K and exposed to N_2, the spectra shown in Figure 6 resulted. The oxidized $Rh^{\delta+}N_2$ species band at 2303 cm^{-1} was detected at all pressures, the physisorbed N_2 species band was present after exposure to N_2 at 9008 Torr, and there was no band detected at 2250 cm^{-1}. The results were similar to those for the oxidized 2.2% Rh/Al_2O_3 catalyst except that the 2276-cm^{-1} band was not resolved for the 0.5% sample. This could indicate that the species causing the 2276-cm^{-1} band is a metallic site present in higher concentration on the 2.2% sample and influenced by oxygen. Upon exposure at 9008 Torr of N_2, the impurity CO produced primarily the gem dicarbonyl species (2035 and 2096 cm^{-1}) and $Rh^{2+}CO$ (2122 cm^{-1}).

Figure 7 shows the result of exposure of 9078 Torr of N_2 to a 0.5% Rh/Al_2O_3 sample which had been pretreated (Experimental Section) so as to produce a reduced surface saturated with the gem dicarbonyl Rh^+ species, with a minimal amount of linear or bridged RhCO species. The only N_2 band which could be detected was the 2328-cm^{-1} one corresponding to physisorbed N_2 on Al_2O_3. The absence of the 2256- and 2300-cm^{-1} bands in this case for chemisorbed RhN_2 species would seem to provide evidence favoring formation of these species on sites preferred by the gem dicarbonyl species, i.e. highly dispersed, rather than metallic sites. This conclusion is in accord with our observations in Figure 5 in which the 2256-cm^{-1} band declined in intensity as the gem dicarbonyl bands grew. However, an alternative hypothesis might be that the 2256-cm^{-1} band was absent because Rh^0 sites were consumed in forming $Rh^+(CO)_2$ and that the 2301-cm^{-1} band was absent because Rh^+ sites were saturated with the gem dicarbonyl species precluding the formation of any Rh^+N_2.[16]

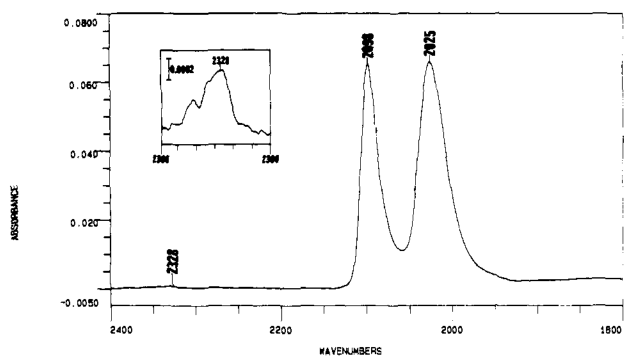

Figure 7. Infrared spectra for 9078 Torr of N_2 interacting with a prereduced 0.5% Rh/Al_2O_3 film which was subsequently exposed to 50 Torr of CO for 5 min at 298 K, held at 1×10^{-6} Torr for 2.5 h at 403 K, and then cooled to 298 K.

The experimental observations in this work cannot distinguish betwen "end-on" and "lying-down" N_2 for the various RhN_2 surface species. However, we agree with the conclusion of Wang and Yates[12] that "end-on" bonding with low inherent extinction coefficients is the most likely even though "lying-down" N_2 species could be infrared active for small metal particles.[17]

Finally, it should be noted that other elegant high-pressure infrared-cell reactors have been reported.[18,19] Peri has reviewed a number of these and concluded that additional work on the subject would be desirable.[18] We believe that the cell reactor described herein is unique in its capabilities in that reactions may be studied at low temperatures (110 K) as well as high temperatures (600 K) and that the pressure range is broad (10^{-8}–10^4 Torr). Actually higher pressures could be achieved limited only by the strengths of the outer CaF_2 windows; the 13 atm limit noted in this paper is due to the use of a capacitance manometer for measurement of pressures only up to 10^4 Torr. Although N_2 gas is not infrared active, we have recently been able to eliminate all gas-phase band contribution for high-pressure CO gas (up to 2000 Torr) in the presence of $CO/Rh/Al_2O_3$ surface species using the short path length reactor and the subtractive capabilities of the FTIR system.

IV. Conclusion

From this work, the following may be concluded: (1) N_2 chemisorbs and physisorbs on Rh/Al_2O_3 catalysts at ambient temperature at pressures above atmospheric; (2) The primary infrared band for reduced Rh/Al_2O_3 occurs at 2256 cm^{-1} and probably should be assigned to an "end-on" RhN_2 species; it is not certain from this work whether this species contains Rh^0 or Rh^+; (3) in the presence of impurity CO, some Rh sites become oxidized giving rise to a $Rh^{\delta+}N_2$ species exhibiting an infrared band at 2301 cm^{-1}; (4) an infrared band at 2276 cm^{-1} for oxidized Rh/Al_2O_3 can probably best be assigned to a metallic Rh site influenced by nearby oxygen; and (5) this work describes a new high-pressure infrared-cell reactor which can be used to monitor surface species under industrial reaction conditions.

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