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# Study of the Reactivity of Chemisorbed CO on Rh/SiO$_2$ Catalyst

The reactivities of chemisorbed CO with gaseous $O_2$, NO, and $H_2$ over 1 wt% Rh/SiO$_2$ have been investigated using infrared spectroscopy and temperature-programmed desorption methods. Three types of CO chemisorbed species $Rh(CO)_2$ (**I**), Rh(CO) (**II**), and $Rh_2(CO)$ (**III**), were found on the silica-supported rhodium catalyst at room temperature. The reactivity of these species with $O_2$ or $H_2$ is in the order of **I** > **II** ≫ **III**. Chemisorbed CO cannot react with gaseous NO, but species **II** and **III** can exchange with NO forming chemisorbed species Rh(NO) and $RhO_2(NO)$ at the cluster $Rh_x$ sites.

## INTRODUCTION

Carbon monoxide is an important reactant in the field of the $C_1$ chemical industry. A number of studies have focused on the use of infrared spectroscopy as a means of probing the interaction of CO with supported Rh catalysts (*1–6*). They found that the behavior of supported rhodium catalysts is quite dependent upon the chemical nature, degree of dispersion, and oxidation state of the rhodium. Recently, Yates *et al.* have reported the activated surface processes of CO chemisorption on supported Rh (*7*). Solymosi and co-workers have worked extensively on methanation of $CO_2$ over various supported Rh catalysts (*8, 9*). Kellner and Bell have shown that the principal oxygenated products of the reaction of $H_2$ and CO over supported ruthenium are acetaldehyde and methanol (*10*). Andersson and Scurrell have investigated by ESCA supported rhodium catalysts related to activity for methanol carbonylation (*11*). Apple and Dybowski (*12*) have employed NMR spectrometry to study the effect of coadsorption of CO and $H_2$ on supported rhodium.

The purpose of this work was to investigate the reactivities of chemisorbed CO with gaseous $O_2$, NO, and $H_2$ over a Rh/SiO$_2$ catalyst. The infrared spectroscopy and temperature-programmed desorption methods have been employed in this study. In order to determine the intermediates present in the course of hydrogenation of chemisorbed CO on the Rh/SiO$_2$ catalyst, infrared spectra for $H_2CO$ adsorption and coadsorption of the $H_2$ + CO mixture were also detected.

## EXPERIMENTAL

The silica-supported rhodium catalyst used in this study was prepared by impregnation according to the incipient wetness procedure. The percentage of Rh by weight based on metal plus support was 1% in all the catalysts. The support used was a porous silica (600 m$^2$/g). The aqueous solution of $Rh(NO_3)_3$ were prepared by dissolving the salt in distilled water. After impregnation the catalyst was dried for 2 days at room temperature and then 2 h in an oven at 393 K. The dried catalyst was reduced in flowing $H_2$ for 2 h at 553 K after which it was kept in a dessicator.

Infrared spectra were obtained using a stainless-steel cell equipped with KBr windows held in place by threaded caps. The cell is connected to a gas handling and vacuum system. Ultimate pressures of $6 \times 10^{-7}$ Torr were obtainable under dynamic conditions. The sample pellets were prepared by pressing about 80 mg of the catalyst in a 2.5-cm-diameter metal die at a pressure of about 1400 kg/cm$^2$. Before the measurements were taken the catalyst pellet was rereduced in flowing $H_2$ at 553 K for 2 h and evacuated for 3 h at the same temperature in the infrared cell. Following

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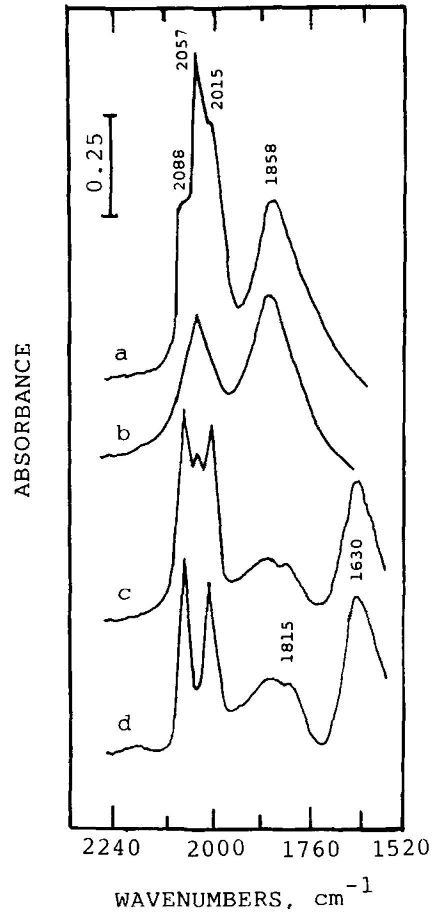


FIG. 1. Spectra of chemisorbed CO reaction with $O_2$ and NO: (a) 10 Torr CO adsorption on $Rh/SiO_2$ catalyst; (b) 3 Torr $O_2$ reaction with preadsorption CO; (c) 4 Torr NO reaction with preadsorption CO; (d) 8 Torr NO reaction with preadsorption CO.

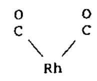
cooling, a background IR spectrum was recorded. All spectra reported have been obtained by ratioing to this background. Dosing of CO, $O_2$, NO, and $H_2$ was carried out by expanding a small volume (0.5 ml) of either gas at 1 atm into the infrared cell.

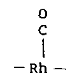
TPD experiments were performed in the same experimental apparatus as mentioned above. The gaseous product distribution of the desorption and reaction was measured by a time-of-flight mass spectrometer. After an IR measurement, helium was led into the infrared cell. The gaseous products of a reaction were analyzed at room temperature in a helium flow rate of 25 $cm^3$/min. For TPD experiments, the catalyst temperature was then increased linearly at a heating rate of 10 K/s. to a final temperature of 773 K in a He flow rate of 20 $cm^3$/min. From the shape and the position of the maxima of a thermal desorption trace, the respective binding state of the adsorbate can be determined. The total desorption peak area reflects the total amount of adsorbed gas.

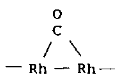
## RESULTS AND DISCUSSION

### *A. Chemisorbed CO Reaction with $O_2$ and NO*

Figure 1a shows the spectrum of CO adsorption on silica-supported rhodium taken at room temperature, 10 Torr dose of CO exposed 1 min then evacuated. It can be seen from Fig. 1a that four bands (at 2088, 2057, 2015, and 1858 $cm^{-1}$) appear in the spectrum. According to the infrared results for this system obtained in the past (*13*), it is believed that three generalized types of chemisorbed CO are produced on silica-supported rhodium catalysts. They are as follows:


(I)
2088-2015 $cm^{-1}$

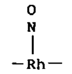

(II)
2057 $cm^{-1}$


(III)
1858 $cm^{-1}$

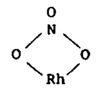
Infrared bands at 2088–2015 $cm^{-1}$, which do not shift with coverage, were assigned to the symmetric and antisymmetric stretching modes of *gem*-dicarbonyl (**I**). The species **I**, $Rh(CO)_2$, occurs on isolated Rh sites. The bands at 2057 and 1858 $cm^{-1}$ were assigned to the linear species **II**, Rh(CO), and bridged species **III** $Rh_2(CO)$, respectively. Both the species **II** and **III** occur on the cluster $Rh_x$ sites. These bands occur at 2100–2030, 2070, and 1870 $cm^{-1}$, respectively, for Rh supported on $Al_2O_3$ (*1–6*).

Figure 1b shows the spectrum was obtained after reaction of chemisorbed CO with gaseous $O_2$, the catalyst of preadsorbed CO exposed to 3 Torr dose of $O_2$ for 1 min. In comparison with Fig. 1a, it is clear that the species **I** was completely annihilated, species **II** was diminished in a degree, and species **III** is almost unaffected by $O_2$. There was no evidence found that chemisorbed $CO_2$ band appears in the spectrum at room temperature. But analytical results of gaseous products indicated that $CO_2$ is the reaction product of chemisorbed CO with $O_2$. It will be seen from these facts that the reactivity of three types of CO chemisorbed species with $O_2$ to form $CO_2$ is in the order of $\mathbf{I} > \mathbf{II} \gg \mathbf{III}$.

Figures 1c and 1d show the spectra were measured after reaction of chemisorbed CO with gaseous NO, the catalyst of preadsorbed CO exposed to 4 Torr dose of NO for 2 min (Fig. 1c) and 8 Torr dose of NO for 2 min then evacuated (Fig. 1d). It is obvious that two new bands occur when NO is added to preadsorbed CO, the band at 1815 $cm^{-1}$ is assigned to Rh–NO and the band at 1630 $cm^{-1}$ to $RhO_2NO$.



1815 $cm^{-1}$



1630 $cm^{-1}$

These bands occur at 1830 and 1660 $cm^{-1}$, respectively, for Rh supported on $Al_2O_3$ (*14*). Exposure of catalyst to NO after preadsorption of CO results in desorption of species **II** which is almost completely removed following a treatment with 8 Torr of NO followed by pumping, compare Figs. 1a and 1d. Species **III** is also markedly altered but may not be removed completely. The *gem*-dicarbonyl, species **I**, is almost unaffected by NO in agreement with previous work (*5, 15*). The apparent increase in the 2088-$cm^{-1}$ half of the doublet is probably attributable to a small amount of $Rh^{1+}$–CO formed by oxidation of $Rh^0$–CO. It is worth noticing that the gaseous products of reaction and desorption are CO and NO only as judged by the mass analysis. It will be seen from this that the bridged $O^{-2}$ in the species $RhO_2(NO)$ may come from the silica support. From the results mentioned above, we can arrive at a conclusion that chemisorbed CO cannot react with gaseous NO, but species **II** and **III** can exchange with NO forming chemisorbed species Rh(NO) and $RhO_2(NO)$ at the cluster $Rh_x$ sites.

### *B. Chemisorbed CO Reaction with $H_2$*

Figure 2b shows the spectrum was taken after reaction of chemisorbed CO with gaseous $H_2$, the catalyst of preadsorbed CO exposed to 4 Torr dose of $H_2$ for 3 min then

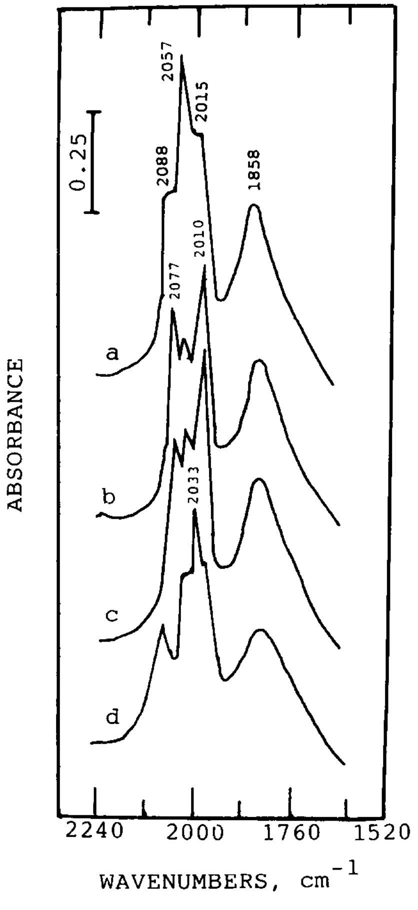
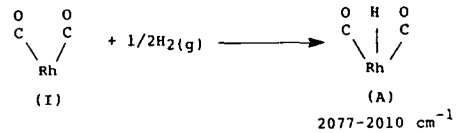


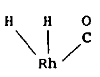
FIG. 2. Spectra of chemisorbed CO reaction with $H_2$: (a) 10 Torr CO adsorption on $Rh/SiO_2$ catalyst; (b) 4 Torr $H_2$ reaction with preadsorption CO; (c) spectrum of coadsorption of the $H_2$ + CO mixture (5 Torr $H_2$ plus 5 Torr CO); (d) spectrum of $H_2CO$ adsorption on $Rh/SiO_2$ catalyst (5 Torr $H_2CO$).

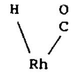
evacuated. The spectrum of chemisorbed CO is also shown in Fig. 2a. From the main difference between the spectrum of adsorbed CO and that obtained after reaction of adsorbed CO with $H_2$, it can be observed that species **I** completely disappeared, species **II** was abbreviated by parts, and two new bands (at 2077 and 2010 $cm^{-1}$) appear in the spectrum. The new band at 2077–2010 $cm^{-1}$ were assigned to the symmetric and antisymmetric carbonyl-hydride species of $HRh(CO_2)$, which occurs on isolated Rh sites. It may be seen that the activity order of hydrogenation of CO chemisorbed species is the same as the oxidation, and the reaction of the species **I** with gaseous $H_2$ is as follows:



It was important to determine whether $H_2CO$ was the intermediate in the course of hydrogenation of chemisorbed CO on silica-supported rhodium. If this were true, then the species $(H)_2Rh(CO)$ or $(H_2CO)Rh$ and $HRh(HCO)$ could be found in the spectra of $H_2CO$ adsorption and coadsorption of the $H_2$ + CO mixture, and $H_2CO$ could be seen in the gaseous products of coadsorption of the $H_2$ + CO mixture.

The IR spectrum shown in Fig. 2c was obtained after coadsorption of the $H_2$ + CO mixture on a freshly prepared silica-supported Rh, where the dosage of the $H_2$ + CO mixture was made equivalent to the $H_2CO(g)$. Figure 2d shows the spectrum taken after $H_2CO$ adsorption on silica-supported Rh; the catalyst was exposed to 5 Torr dose of $H_2CO$ for 3 min then evacuated. It is obvious that the spectrum of coadsorption of the $H_2$ + CO mixture is analogous to that observed for the hydrogenation of chemisorbed CO. As distinguished from the behavior of coadsorption of the $H_2$ + CO mixture, a new band (at 2033 $cm^{-1}$) appears in the spectrum of $H_2CO$ adsorption except the adsorbed species **II**, **III**, and **A**. This band at 2033 $cm^{-1}$ was assigned to the carbonyl-hydride species of HRh(CO). The species of $(H)_2Rh(CO)$, $(H_2CO)Rh$, and HRh(HCO) were not observed to form in detectable amounts in any of the spectra measured in our experiments. This result is in agreement with the earlier results obtained for single rhodium atoms (*16*). For the coadsorption of the $H_2$ + CO mixture, the results of TPD indicated that gaseous $H_2CO$ was not present in the reaction products.

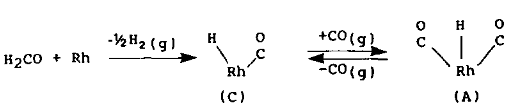

(B)
2023 $cm^{-1}$


(C)
2033 $cm^{-1}$

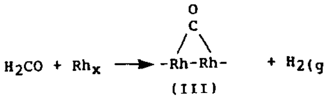
It can be seen from these experimental facts that $H_2CO$ is not a relevant intermediate in the course of hydrogenation of chemisorbed CO on silica-supported rhodium.

Based on the results mentioned above, we suggest that the following surface processes occur when $H_2CO$ adsorbs on silica-supported rhodium catalyst.

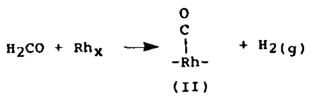
Isolated Rh atom sites



cluster $Rh_x$ sites



and



Allied to these surface processes, it has been found that the gaseous $H_2$ exists in the reaction product when $H_2CO$ dissociative chemisorption on $Rh/SiO_2$ catalyst.

## CONCLUSIONS

This investigation has shown that the reactivity of CO chemisorbed species is quite dependent upon their chemical nature, the degree of dispersion, and oxidation state of silica-supported rhodium. Three types of CO chemisorbed species, $Rh(CO)_2$ (**I**), Rh(CO) (**II**), and $Rh_2(CO)$ (**III**) were found on the $Rh/SiO_2$ catalyst. In respect to the reactivity of these species with gaseous $O_2$ to form $CO_2$, the most active one is species **I** and the most stable one is the species **III**. As distinguished from the oxidation of three species, species **I** cannot react with gaseous NO, but species **II** and **III** can exchange with NO forming chemisorbed species Rh(NO) and $RhO_2(NO)$ at the cluster $Rh_x$ sites. The reactivity of CO chemisorbed species with gaseous $H_2$ is in the order of $\mathbf{I} > \mathbf{II} \gg \mathbf{III}$. The species $(H)_2Rh(CO)$ or $(H_2CO)Rh$ and HRh(HCO) were not found on the $Rh/SiO_2$ catalyst in the experiments of $H_2CO$ adsorption and coadsorption of the $H_2$ + CO mixture. Gaseous $H_2CO$ did not present in the reaction products of coadsorption of the $H_2$ + CO mixture. It follows that $H_2CO$ is not relevant to the intermediate in the course of hydrogenation of chemisorbed CO over $Rh/SiO_2$ catalyst.

## REFERENCES

1. Yates, J. T., Duncan, T. M., Worley, S. D., and Vaughan, R. W., *J. Chem. Phys.* **70,** 1219 (1970).
2. Worley, S. D., Rice, C. A., Mattson, G. A., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Phys. Chem.* **88**(14), 2714 (1982).
3. Worley, S. D., Rice, C. A., Mattson, G. A., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **74,** 6487 (1981); **76**(1), 20 (1982).
4. Guerra, C. R., and Schulman, J. H., *Surf. Sci.* **7,** 229 (1967).
5. Resasco, D., and Haller, G. L., *J. Chim. Phys.* **78,** 971 (1981).
6. Yates, D. J. C., Marrell, L. L., and Prestridge, E. B., *J. Catal.* **57,** 41 (1979).
7. Yates, J. T., Duncan, T. M., and Vaughan, R. W., *J. Chem. Phys.* **71**(10), 3908 (1979).
8. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Chem. Soc. Faraday Trans.* **77,** 2645 (1981).
9. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981); **70,** 451 (1981).
10. Kellner, C. S., and Bell, A. T., *J. Catal.* **71,** 288 (1981).
11. Andersson, S. L. T., and Scurrell, M. S., *J. Catal.* **71,** 233 (1981).
12. Apple, T. M., and Dybowski, C., *J. Catal.* **71,** 316 (1981).
13. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61,** 1504 (1957).
14. Arai, H., and Tominaga, H., *J. Catal.* **43,** 131 (1976).
15. Unland, M. L., *J. Catal.* **31,** 459 (1973).
16. Yates, J. T., Worley, S. D., Duncan, T. M., and Vaughan, R. W., *J. Chem. Phys.* **70,** 1225 (1979).

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